

Characterization of Particulate Emissions from Diesel Engines

*A Thesis Submitted
in Partial Fulfillment of the Requirements
for the Degree of*

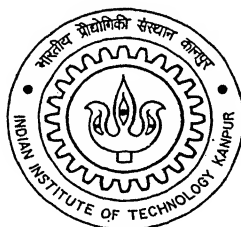
MASTER OF TECHNOLOGY

In

Environmental Engineering and Management

By

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to the

**DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR**

July, 2004

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It is certified that the work contained in the thesis entitled “**Characterization of Particulates Emissions from Diesel Engines**”, by K.V.L.Bharathi, has been carried out under our supervision and that this work has not been submitted elsewhere for the award of a degree.



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Dedicated to,
My parents, brother and friends

ACKNOWLEDGEMENTS

I sincerely express my deep sense of gratitude and regards to my thesis supervisors, Dr. Mukesh Sharma and Dr. A.K. Agarwal for their inspiration, guidance and encouragement throughout the course of my thesis work, which made me realize the importance of this research work.

I am also very thankful to my teachers, Dr. Malay Chaudhuri, Dr. Vinod Tare, Dr. D.K. Ghosh, Dr. Purnendu Bose, Dr. Saumyen Guha and Dr. Binayak Rath for their help and guidance. I am indebted to all of them and IIT Kanpur for giving me the fundamentals and chance to implement them.

I am very much thankful to Environmental Engineering Laboratory staff and Energy Conversion Lab staff for their timely help and guidance.

I express my special thanks to my dear friends for their continuous support, suggestions and love. Long discussions on various subjects with them had helped me to develop my personality and knowledge.

I have no words to express my respect for my parents and my family members who have been constant source of inspiration to me. I wish to thank all my friends and well wishers who made my stay at IIT Kanpur, memorable and pleasant.

Bharathi

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ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
APHEA	Air Pollution on Health: a European Approach
ARB	Air Resource Board
BSOF	Benzene Soluble Organic Fraction
CAL EPA	California Environmental Protection Agency
DPM	Diesel Particulate Matter
EC	Elemental Carbon
HEI	Health Effects Institute
HPLC	High Performance Liquid Chromatography
IC	Inorganic Carbon
IARC	International Agency for Research on Cancer
IITK	Indian Institute of Technology, Kanpur
MDS	Microwave Digestion System
NAAQS	National Ambient Air Quality Standards
PAH	Polycyclic Aromatic Hydrocarbons
PM	Particulate Matter
PM₁₀	Particulate Matter of aerodynamic diameter less than 10 micron
PM_{2.5}	Particulate Matter of aerodynamic diameter less than 2.5 micron
SAE	Society of Automotive Engineers
TC	Total Carbon
TOC	Total Organic Carbon
USEPA	United States Environmental Protection Agency

ABSTRACT

This study was set out to characterize particulate emissions from diesel engines in terms of Heavy metals, Benzene Soluble Organic Fraction, Elemental and Organic Carbon and Polycyclic Aromatic Hydrocarbons (PAHs). The Heavy metal content in particulates was correlated with that of metal content in diesel and lubricating oil. For this study, the exhaust from Mahindra DI engine was analyzed for the above parameters at three different engine loading conditions namely idle, 40%, 70% and 100%. It was found that as the load is increased from idle to 100% the heavy metal content in particulates gradually decreased. It was found heavy metal content was maximum at idle condition revealing that this would be due to inadequate combustion of diesel and lubricating oil. It is evident that the major source of heavy metals in particulates are from diesel and lubricating oil, while some metals are due to wear of engine components. Benzene Soluble Organic Fraction, which is a marker for carcinogenicity, also showed decrease in levels with increase in load. It was found that at idle condition 67% of organic fraction was soluble in Benzene with a minimum of 25 % at 100 % load. Elemental Carbon levels increased with increase in load showing a maximum of 48 % EC at 70% load with a minimum of 25 % at idle condition. The trend of Organic Carbon was quite opposite, it showed 35 % OC at idle condition and decreased gradually with increase in load. In case of PAHS, the Concentration of Chrysene, Benzo (k) Fluoranthene, Benzo (a) Pyrene, Dibenzo(a,h)Anthracene and Benzo(g,h,i) Perylene were found to increase with increase in load from idle to 40% load and decreased further upon reaching 70 % load.

Chapter 1

INTRODUCTION

Diesel engine is a type of internal-combustion engine invented and patented by the German engineer Rudolf Diesel in 1892. Diesel engines are a major source of particulate emissions, which mainly consist of soot with additional Polycyclic Aromatic Hydrocarbons, Heavy metals and Nitrogen Oxides. Diesel engines have been used increasingly in various industries since 1930s. Today, they form power plants for railroad locomotives, heavy equipment and vehicles, buses, trucks and cars apart from stationary power generation. They are also used extensively in mining and dock operations. They are widely used in mobile and stationary installations where power requirement is between that furnished by small gasoline engine (few kilowatts) and that of the steam turbine (in megawatts) and where relatively high initial cost can be written off over a long period. For example, diesel engines having capacities of 100 to 5,000 hp are employed on industrial and municipal electric generators and on continuously operating pumps (e.g., on oil pipelines). Diesel engines are Robust and highly reliable source of power generation. Diesel engines are available in two stroke as well as four-stroke cycles.

Diesel engines are considered safer than Gasoline engines. Gasoline engine exhaust poses a greater carbon monoxide hazard than diesel. Diesel exhaust produces about 70% less carbon monoxide than its gasoline counterpart. This is not a significant for power plants, as they are located in remote places where as this is an important consideration for generators. Another aspect of diesel exhaust to be considered is sulfur dioxide content.

Diesel engines use less amount of fuel than gasoline engines. This is due to their higher efficiency because of their higher compression ratios. Another reason is their ability to burn extremely lean mixtures of fuel and air. Diesel engines offer excellent fuel mileage, durability, and torque compared to that of their conventional gasoline fueled counterparts, hence these engines are getting more and more popular. Diesel engines last longer than gasoline engines. A diesel engine is more strongly constructed in order

to withstand the higher compression ratios and peak cylinder pressures. Today the consumption of diesel fuel is 5-6 times higher than the gasoline consumption worldwide. Hence it becomes extremely important to investigate and control the diesel engines emissions more carefully.

1.1 Diesel Engine Exhaust

Diesel Engine Exhaust is a complex mixture containing several organic and inorganic gaseous species and particulates, formed during combustion process. Diesel engine emits gaseous pollutants and carbonaceous matter typically described as diesel particulate matter (DPM). The gaseous pollutants contain nitrogen oxides, carbon dioxide, carbon monoxide and many toxic substances including aldehydes. Oxides of nitrogen, which are ozone precursors, are among the combustion products in the gaseous phase. The particulate matter consists of an elemental carbon core with several organic compounds, sulfates, nitrogen oxides, heavy metals, trace elements and irritants (such as acrolein, ammonia, acids, fuel vapors, unburnt lubricating oils, moisture) absorbed to its surface. Specific toxic chemicals of concern adsorbed by particulate matter include Polycyclic Aromatic Hydrocarbons (PAH's) and nitroarenes [1]. EPA approximated that 90% of diesel particles have diameter less than 1 micron and at least 94% are less than 2.5 microns [1,2].

The particle size distribution and chemical composition of diesel exhaust emissions can vary greatly depending on the engine type, engine speed and load, fuel composition, lubricating oil type and emission control technology [1]. The mass, composition and particle size distribution of diesel exhaust has changed with in last 30 years because of improvements in engine technologies, controls and fuel formulation. For example, with development of engine technology in early 1990's the emissions (by mass) of Nitrogen oxides and Particulate matter from on-road diesel engines were much lower than in older engines because of significant advancement in exhaust after treatment technologies [2]. With the advancement in capabilities to conduct toxicology studies, the concern for harmful health effects from diesel engines has increased worldwide.

Diesel exhaust particles are primarily associated with particulate matter smaller than 2.5 microns ($PM_{2.5}$). Engines contribute to significant amount of $PM_{2.5}$ to the ambient

air, particularly in urban areas. EPA estimated that the fraction of diesel particulate matter in $PM_{2.5}$ is typically in the range of 10 percent though it may go up to 30 percent in some urban settings [3].

Despite the lower particulate mass emissions from newer engines, it is not yet clear whether the hazard from diesel particulates has similarly decreased, in other words whether the diesel emissions are less toxic [1]. Total mass may not be the best descriptor of health effects. If technology improvements lead to a larger number of smaller particles, with greater surface areas and depositional efficiency, then it is conceivable that the hazards could actually increase with engine technology improvements. The health implications of the potentially higher numbers of ultra fine diesel particles (less than $0.01\ \mu m$) are not yet known [4]. Diesel engines are highly durable power plants and a large number of older engines are still in use today, further complicating the pollution problems. In addition, diesel fuel consumption is expected to increase worldwide. EPA concluded that it is not yet clear if the risk of diesel emissions has decreased over time [3]. Since it is clearly established that diesel exhaust is harmful for public health and the degree of toxicity of the exhaust is function of particle size and its chemical composition, which itself is uncertain due to changes in technology, there is a need to study both emission of particulate matter and its chemical composition from diesel exhaust.

1.2 Objectives of the Study

The diesel exhaust for the purpose of toxicity characterization needs to be studied for the following parameters:

1. Metal Content
2. Elemental Carbon Content
3. Organic Matter in terms of Benzene Soluble Fraction (BSF)
4. Carcinogenic Polycyclic Aromatic hydrocarbons (PAH's)

Therefore, the objectives of the present research are to characterize the diesel exhaust particulate matter for above four parameters under varying engine conditions/loads.

Chapter 2

LITERATURE REVIEW

The internal combustion engine has been the main workhorse of shaft power since the early part of 20th century. Their light, compact design and easy availability of relatively cheap petroleum fuels ensured that the internal combustion engines quickly replaced the bulkier steam engines. Huge number of internal combustion engines have since been produced worldwide and vast majority have been fitted in motor vehicles, and other diverse applications such as powering electricity producing generators, ships and boats, agricultural and agro processing machinery and many industrial applications. They are extremely versatile with a very high power to weight ratio. However they create lot of pollution because they emit particulate matter and several gaseous pollutants. Several countries worldwide have adopted emission legislations to curb health problems generated by Internal Combustion Engines. Many countries have adopted strict ambient air quality standards in order to control the exposure of its citizens to the harmful pollutants and reduce health risks.

2.1 Automotive Emissions

The operation of diesel engines creates five major categories of emissions. They are listed below;

Greenhouse gases describe a variety of emissions that, while not generally harmful to living organisms, trap heat within the earth's atmosphere. Large quantities of greenhouse gasses in the atmosphere are said to be the primary cause of global warming. Carbon dioxide is the most prevalent greenhouse gas in automotive emissions.

Noxious gasses represent the second variety of automotive emissions. Even in small quantities, noxious gasses pose an immediate health hazard to living organisms. The most significant automotive noxious gasses are sulfur dioxide, oxides of nitrogen and carbon monoxide. Sulfur dioxide and oxides of nitrogen are commonly associated with

photochemical smog, that brown haze that is sometimes seen over major industrial areas. Carbon monoxide is a colorless, odorless gas that displaces oxygen in blood's hemoglobin.

Unburned hydrocarbons represent the third category of automotive emissions and consist of the gasoline and lubricating oil that remains burnt during the combustion process. When introduced into the environment, these unburned hydrocarbons will either breakdown into smog-forming chemical compounds or get into the water table.

Particulate, or soot, is the fourth category of automotive emissions. Most frequently associated with diesel engines, soot consists of microscopic carbon-based particles that irritate mucous membranes and are thought to be a significant contributor to the growing asthma problems primarily noticed in industrial world.

Water is the fifth, and most frequently overlooked, variety of automotive emissions. Although not in itself toxic, water can combine with greenhouse and noxious gasses to form acids. Fig 2.1 gives summary of on-road diesel emission standards.

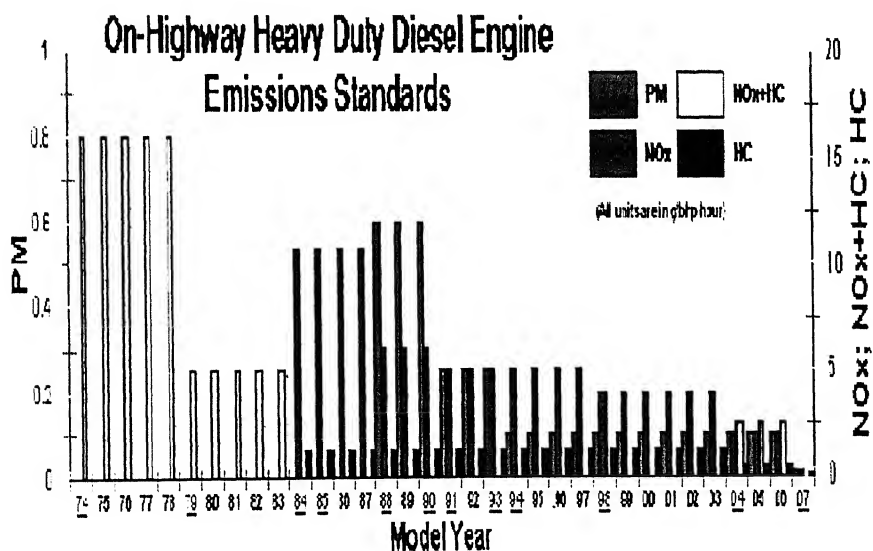


Fig 2.1: Summary of On-road Diesel Emission Standards [13]

The Table 2.1 refers to Major Criteria Pollutants from Diesel source Categories and Fig 2.2 gives contribution of various sources towards NO_x.

Table 2.1: Major Criteria Pollutants from the Four Most Important Diesel Source Categories in 2000 (does not include air toxics) [3]

Source/Pollutant (tons X 1000)	CO	NO _x	SO ₂	VOC	PM ₁₀	PM _{2.5}
On-road diesel	2,234	3,312	118	260	168	147
Non-road diesel	1,242	2,660	516	342	241	222
Marine diesel	141	1,090	872	32	42	39
Railroad	119	1,230	56	48	30	27

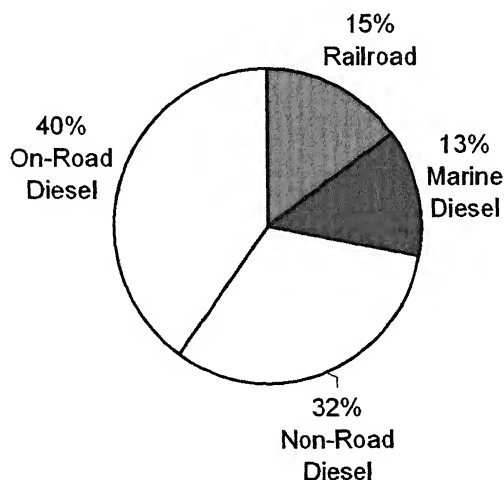


Fig 2.2: Diesel NO_x by Source Category in 2000. On-road Diesel Comprised the Largest Share [13]

2.1.1 Vehicular Emission Norms

The following emission standards apply to new diesel engines used in heavy-duty highway vehicles. Model year 1988-2003 US federal (EPA) and 1987-2003 California

(ARB) emission standards for heavy-duty diesel truck and bus engines are summarized in the following tables (Table 2.2 and 2.3). Applicable to the 1994 and following year standards, sulfur content in the certification fuel has been reduced to 500 ppm by weight [12].

Table 2.2: EPA Emission Standards for Heavy-Duty Diesel Engines, g/bhp-hr [12]

Year	HC	CO	NO _x	PM
Heavy- Duty Diesel Truck Engines				
1998	1.3	15.5	10.7	0.6
1990	1.3	15.5	6.0	0.6
1991	1.3	15.5	5.0	0.25
1994	1.3	15.5	5.0	0.1
1998	1.3	15.5	4.0	0.1
Urban Bus Engines				
1991	1.3	15.5	5.0	0.25
1993	1.3	15.5	5.0	0.1
1994	1.3	15.5	5.0	0.07
1996	1.3	15.5	5.0	0.05
1998	1.3	15.5	4.0	0.05

Table 2.3: California Emission Standards for Heavy-Duty Diesel Engines, g/bhp-hr [12]

Year	NMHC	THC	CO	NO _x	PM
Heavy- Duty Diesel Truck Engines					
1987	-	1.3	15.5	6.0	0.6
1991	1.2	1.3	15.5	5.0	0.25
1994	1.2	1.3	15.5	5.0	0.10
Urban Bus Engines					
1991	1.2	1.3	15.5	5.0	0.10
1994	1.2	1.3	15.5	5.0	0.07
1996	1.2	1.3	15.5	4.0	0.05

2.2 Particulates

The U.S. Environmental Protection Agency (EPA) has revised the particulate air quality standard by adding two $PM_{2.5}$ standards set at $15 \mu\text{g}/\text{m}^3$, annual mean and $65 \mu\text{g}/\text{m}^3$, 24 hour average. The EPA also retained the annual primary PM_{10} standard of $50 \mu\text{g}/\text{m}^3$ [11] EPA believes that attainment of these standards will provide increased protection against a wide range of health effects associated with particulate matter (PM). The European commission proposed a similar ruling that will tighten ambient PM requirements and mandate increased monitoring of PM_{10} and $PM_{2.5}$. This was encouraged by a series of studies called the APHEA studies, which paralleled the U.S results. The standards proposed for particulate are shown in Table 2.4. Both proposals focused increased attention on the need for PM control.

Table 2.4: Particulate Standards Proposed by European Commissions [13]

	Averaging Period	Limit value $\mu\text{g}/\text{m}^3$	Implementation Dates
PM_{10}	24 hours	50 25 X year	2005
PM_{10}	Annual	30	2005
PM_{10}	24 hours	50 7X year	2010
PM_{10}	Annual	20	2010

2.2.1 Formation of Particulate Matter

Studies have shown that the primary soot particles in diesel exhaust are formed in the combustion chamber by nucleation of heavy relative molecular weight PAH [14], with a large percentage of these being oxidized during the expansion stroke [15]. The particles that survive oxidation typically agglomerate together to form the long chain aggregates or clusters associated with diesel particles. The final particle processes occur in the atmosphere. These are mainly photochemical reactions and to a lesser extent particle surface reactions. It is also possible to have gas-to-particle conversion due to the nucleation of hydrocarbons, oxides of nitrogen, or oxides of sulfur [16]. The various stages of soot formation are shown in Fig 2.3 and explained below,

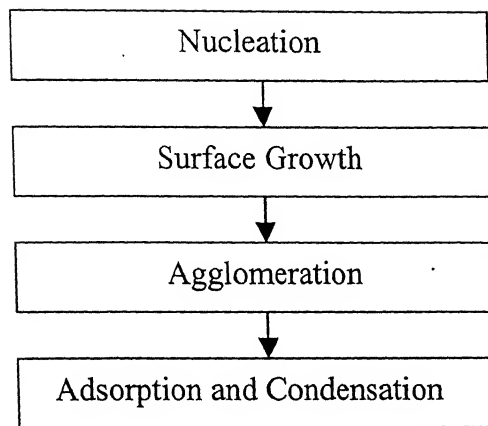


Fig 2.3: Formation of Particulate Matter in Diesel Engines

1. Particle formation, where the first condensed phase material arises from the fuel molecules via their oxidation and/or pyrolysis products. These products typically include various unsaturated hydrocarbons, particularly acetylene and its higher analogues ($C_{2n}H_2$), and Polycyclic aromatic hydrocarbons (PAH). These two types of molecules are considered the most likely precursors of soot in flames. The condensation reactions of gas-phase species such as these lead to the appearance of the first recognizable soot particles (often called nuclei). These first particles are very small ($d < 2\text{nm}$) and the formation of large numbers of them involves negligible soot loading in the region of their formation.

2. Particle growth, which includes surface growth, coagulation, and aggregation. Surface growth, by which the bulk of the solid-phase material is generated, involves the attachment of gas-phase species to the surface of particles and their incorporation into the particulate phase. Nucleation and condensation are gas-to-particulate conversion processes, while coagulation is a pure interaction between particulates. The driving force for this gas to particulate conversion process is the saturation ration. Condensation is similar to the nucleation process except that the volatile materials condense on existing particulate, resulting in an increase in mass concentration of the particulate. Coagulation occurs when the particulates come into contact with each other under the influence of the Brownian force, resulting in a reduction in the number

concentration of the particulate. In summary, nucleation contributes to the formation of new particulates; condensation contributes in an increase in particulate size, while coagulation leads to an increase in particulate size but a reduction in the number of particulates.

2.3 Particulate Composition

The particles emitted from diesel engines are mainly aggregates of spherical carbon particles coated with organic and inorganic substances with the composition of the particles (Fig: 2.4) being predominantly, 80 to 90 percent, organic and inorganic carbon [17]. The inorganic fraction consists of small solid carbon particles, ranging from 0.01 to 0.08 micrograms, and sulfur, oxygen, carbon, sulfate (SO_4), CO and NO_x [14]. The amount of the solid carbon, or EC, in the average particle will typically range from approximately 64 percent to 71 percent [18].

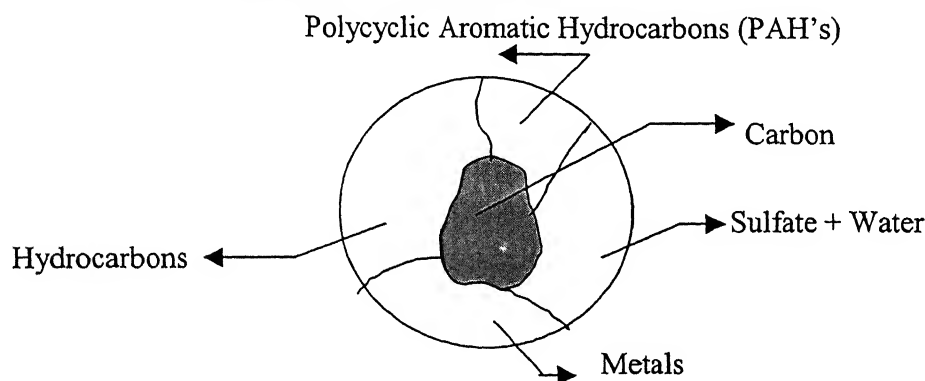


Fig 2.4: Composition of Particulate matter

The fine EC aerosol is formed during the combustion process, and is not found in the atmosphere by reactions involving gaseous hydrocarbon precursors. Therefore, the entire concentration of EC observed in the atmosphere is from primary emission sources. The characteristic sponge-like structure and large surface area (50 to 200 mg/gram of soot: [18] of particles emitted from diesel engines make it an excellent carrier for organic compounds of low volatility. These compounds reside on the particle surface (as a liquid) or are included inside the particle, or both. Organic compounds present inside the particles may be protected against photolysis and

chemical reaction, while organic compounds present on the surface of the particles can volatilize or react with other compounds from the particle surface.

The organic fraction of the diesel particle contains compounds such as aldehydes, alkanes and alkenes, aliphatic hydrocarbons, and PAH and PAH-derivatives [4]. The organic fraction comes from the unburned fuel and lubricating oil, and from partially oxidized fuel and oil [19]. The majority of the organic fraction is adsorbed onto the surface of the solid carbon core. This fraction is called the soluble organic fraction (SOF) because of its solubility in solvents such as dichloromethane [20]. Also associated with the total particle mass (TPM) of the particulate matter may be droplets of liquid, condensed hydrocarbons, and SO_4 particles [14]. These hydrocarbons collected with the TPM are not volatile enough to exist in the vapor phase and may not be adsorbed onto the solid fraction due to low solid levels, but will also be removed by an organic solvent as the SOF [14]. The National Research Council (1983) has shown that approximately 25 percent of the particle mass may be extracted using organic solvents but, depending on the engine conditions and testing cycle, the contribution of organics to the TPM is between 10 and 90 percent [22]. The SO_4 fraction of diesel exhaust TPM is composed primarily of the sulfuric acid formed when sulfur trioxide reacts with water vapor [23]. SO_3 is formed from the oxidation of SO_2 , which is produced during the combustion process by the oxidation of sulfur in the fuel [20]. This portion can contribute up to 14 percent of the diesel exhaust particle [17]. Table 2.5 depicts this information.

Table 2.5: Typical Composition of Particulate Matter

C	31 %
Sulphate & water	14%
Unburned fuel	7%
Unburned Oil	40%

Recently, a study conducted by Bagely et al. [24] characterized the physical and chemical composition of emissions from a 1988 heavy-duty diesel engine equipped

with a ceramic particulate trap, and a 1991 heavy-duty diesel engine equipped with an oxidation catalytic converter. The investigators determined the number and size of particles within the exhaust of the two engines tested. The results show that despite a substantial reduction in the weight of the total particulate matter, the total number of particles from the more advanced 1991-model engine was 15 to 35 times greater than the number of particles from the 1988 engine when both engines were operated without emission control devices. This suggests that more fine particles, a potential health concern, could be formed as a result of new technologies. Further study is needed since the extent of these findings only measured exhaust from two engines and engine technologies.

2.4 Health Effects

Diesel exhaust is a major of several sources of fine particulate matter and gaseous pollutants. It is difficult to distinguish specific health effects of diesel engine emission exposures from those of other pollutants [5]. Lung is a primary organ, which is adversely affected by diesel engine exhaust. Because of their small diameter, diesel particles are readily inhaled and deposited deeply inside the lung. Information from previous studies of occupational exposures suggests that workers exposed to elevated diesel exhaust concentrations have suffered from bronchitis, changes in lung functions and lung cancer [3]. In contrast to its potential for causing lung cancer, the non-cancerous effects of diesel exposures include asthma, respiratory airway inflammation and allergic responses [5].

The health effects of diesel exhaust have been critically assessed by several groups. In 1981, the NRC of the National Academy of Sciences found no evidence for a carcinogenic effect of diesel exhaust in epidemiological studies, although the lack of high-quality research in this area was acknowledged [6]. The National Institute for Occupational Safety and Health suggested that diesel exhaust is a potential human carcinogen [7]. The International Agency for Research on Cancer concluded in 1989 that based on the evidence from animal studies, "Diesel engine exhaust is probably carcinogenic to humans" [8]. The U.S. Environmental Protection Agency in 1992 proposed classifying diesel exhaust as a probable human carcinogen [9].

These evaluations were based primarily on results of experimental animal studies and elevated standardized mortality ratio statistics of lung cancer in some diesel-exposed workers. The epidemiological studies were conducted on truck and other motor vehicle drivers, traffic controllers, coal miners, construction workers, railroad union members and dockworkers [10]. These investigations lacked accurate exposure information on diesel exhaust and individual smoking habits or had insufficient follow-up times to account for the potential latent effects of diesel exposure.

2.5 Summary of Research Studies on Diesel Engine Emissions

Diesel engine exhaust particles have received attention by large number of researchers because they may cause several adverse health effects on urban populations. To date, the International Agency for Research on Cancer (IARC) has classified diesel exhaust emission elements as *probable carcinogens* [25].

Sjogren (1996) conducted study to investigate the mechanisms associated with pulmonary carcinogenicity caused by diesel exhaust particulates [26]. Diesel exhaust also contains various heavy metal contents attached to fine granular matters [27]. Because of their fine particle sizes, they can penetrate into the deep respiratory track and cause respiratory diseases. Valavanidis et al. (2000) indicated that the deposition of metals (especially Fe) on the lower airway firstly would generate hydroxyl radicals then trigger the production of oxygen free radicals and finally cause both acute and chronic lung injuries [28]. Therefore it is expected that, beside the organic contents and particulate matters, the investigation of metal contents in the diesel exhaust is important for assessing health effects associated with diesel emission.

Kittelson (1998), Kerminen and Vilhuene (1997) and Morawska (1998) have conducted many studies to investigate the particle size distribution and particle number concentration and organic matters associated with diesel emissions[29-31] .

2.6 Studies Related to Characterization of Emissions from Diesel Engines

As it is proposed to characterize emissions from diesel engine, a detailed literature survey was undertaken on previous studies conducted by researchers across the world on the following topics.

1. Heavy metals in diesel engine emissions
2. Heavy metals in diesel oil and lubricating oil
3. Benzene soluble organic fraction (BSOF) in diesel engine emissions
4. Elemental and Organic carbon in diesel engine emissions
5. PAH's in diesel engine emissions

Heavy Metals in Diesel Engine Emissions

Hare (1977) found that the metallic elements emitted from the four stroke heavy duty engine include silicon, copper, calcium, zinc and phosphorous, whereas in two stroke engines the metallic elements in emission include were lead, manganese, chromium, zinc and calcium. Calcium, phosphorous and zinc are normally present in engine lubricating oil [32]. The two-stroke engine emits higher lubricating oil generated emissions and therefore emits higher levels of zinc, calcium and phosphorous when compared to four stroke engines.

Springer (1979) found that calcium was the dominant metallic element in diesel particulate matter (DPM), with levels ranging from 0.01 to 0.29 % (w/w). Phosphorous, silica and zinc were the next most abundant metallic elements reported, and sodium, iron, nickel, barium, chromium and copper were either present at very low levels or were below detection limits [33].

Lowenthal et. al. (1994) also reported various metallic emission rates for a composite sample of several diesel vehicles. The most abundant metals were zinc, iron, calcium, phosphorous, barium and lanthanum. The total emission metals were less than 0.3 percent of total DPM mass, with an emissions rate of 1.65 mg/km [17].

Norbeck et. al. (1998) reported engine transient test emissions of metals for a medium duty truck Silicon, iron, zinc, calcium and phosphorous were observed and together

constitute up to about 0.5 percent of total Diesel Particulate Matter with and emissions rate of 1.02 mg/km [34]. Table 2.6 shows the summary of these studies .

Table 2.6: Summary of Various Studies on Vehicular Exhaust Emissions

Researchers	Engine Type	Major metals detected	Metals in traces detected	Total metal content % of DPM (w/w)	Emission rate of metals (mg/km)
Hare (1997)	Heavy duty , diesel, 4 Stroke	Si, Cu, Ca, Zn, P	Ni, V, Pb	-	-
Hare (1997)	Medium duty diesel, 2Stroke	Pb, Mn, Cr, Zn, Ca, P	Ni, V, K	-	-
Springer (1979)	Heavy duty truck, 4 Stroke	Ca, P, S, Zn	Na, Fe, Ni, Ba, Cr, Cu	1	-
Lowenthal et.al. (1994)	Composite samples of various sizes of 4Stroke diesel engines	Zn, Fe, Ca, P, Ba, Lt.	-	0.3	3.3
Norbeck et. al. (1998b)	Medium duty truck (4Stroke, diesel)	Si, I, Zn, Ca and P	-	0.5	1.8

It has been inferred from the studies mentioned in the previous discussion and tables that the major elements emitted from diesel engines are Ca, Mg, Zn, Ba, Pb, Cr, and Ni. Hence in this study Fe, Mg, Cr, Ni, Pb, Zn, Ca and Ba has been selected for investigation.

Heavy Metals in Diesel and Lubricating Oil

Metal content in diesel oil varies depending on the type of diesel oil. However, it should also be noted that the metal contents in lubricant oil could play important roles on the emission of metal contents in engine exhaust particularly for Ca and Zn. Examination of the concentration of various metals in used lubricating oils is thought to be an effective and practical means of monitoring engine wear often giving an early indication of a component failure.

The contribution of lubricating oil to diesel exhaust PM emissions can be substantial. Researchers have reported that from 2 to 48 percent of diesel exhaust particulate matter emissions, depending on speed and load, consisted of material from lubricating oil. Of this material, lubricating oil can contribute up to 88 percent of the SOF of a diesel exhaust particulate matter [35,36,22]. This contribution is important since several studies show that portions of the SOF of the diesel exhaust particles contain substances which are mutagenic, carcinogenic, or both [37-40].

The concentration of certain metals in lubricating oils can be determined. AAS is the most often used analytical method for the determination of metals. The Lubricating oil itself presents handling difficulties, as it is in the form of an extremely viscous liquid. In the literature a number of analytical procedures have been described. Barnooti determined Cr, Fe, Mg and Pb in used lubricating oils using flame AAS after three types of sample preparations namely, direct dilution with an organic solvent, dry ashing followed by acid dissolution and dry ashing in the presence of a porous inert material (silica gel). In the present study it is proposed to analyze diesel oil samples for Fe, Mg, Pb, Zn, Cr, Ni, Al, Ca and Ba, whereas lubricating oil samples are analyzed for Zn, Mg, Fe, Pb, Ca and Ba.

Benzene Soluble Fraction (BSOF) in Diesel Particulates

One of the other objectives of the study is to quantify the hazardous nature of diesel engine exhaust. A detailed study conducted by USEPA (1995b) showed that diesel soot contains many organic compounds and some of them are toxic in nature [41]. The study also concluded that the organic fraction containing neutral and aromatic fraction of diesel soot is mutagenic and carcinogenic in nature.

Crebelli (1991) established a relation between mutagenicity of diesel particulate matter with ambient air samples and BSOF of diesel particulate matter and ambient particulate matter [42]. Under this study the mutagenicity spectra of the organic extracts of both airborne particulate matter and diesel and gasoline soot particles were determined using a battery of nine bacterial strains of different genetic specificity. The assays with crude extracts and with fractionated acidic, neutral and basic components revealed striking differences in the patterns of mutagenic responses produced by each of the complex

mixtures. The mutagenicity of air particulate matter was shown to depend mainly on neutral compounds. It has been reported that the BSOF of PM_{10} in the ambient air samples was found to vary between 12 and 23 % (w/w).

Above-mentioned studies confirmed that the BSOF fraction of diesel engine exhaust represents the aromatic and neutral compounds, which are proved to be carcinogenic in nature. Therefore, in the proposed study, BSOF has been considered as a good representative of mutagenic activity of the emissions from diesel engines hence it is proposed to analyze BSOF in diesel exhaust particulates.

Elemental and Organic Carbon in Diesel Engine Emissions

Studies conducted by USEPA (1995b) showed that the major portion of the vehicular exhaust soot would be the carbon and hence it is proposed to analyze the carbon content in the diesel engine exhaust samples [41]. Carbon in the environmental samples is present in three different forms) :(i) elemental carbon (EC) (ii) inorganic carbon in the form of carbonates and bicarbonates (IC) (iii) organic carbon (OC), as shown in Fig 2.5.

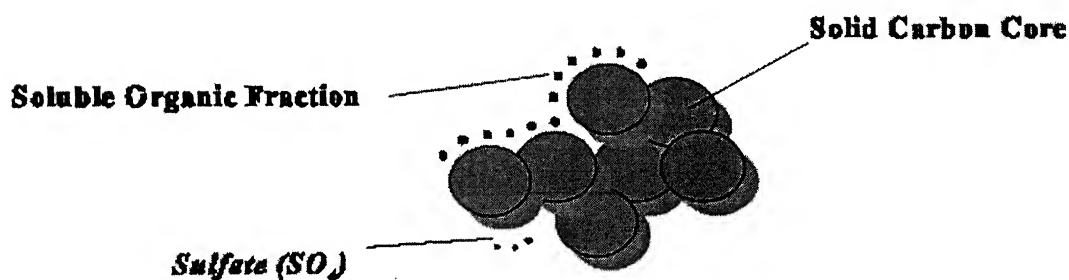


Fig 2.5: Diesel Particulates are Mainly Aggregates of Carbon Particles

Particulate emissions from diesel engines constitute predominantly elemental carbon (EC) and organic carbon (OC). The elemental fraction stems from fuel droplet pyrolysis, while the organic fraction originates from unburned fuel, lubricating oil and combustion by-products. Diesel engines are believed to be the major source of EC in

the atmosphere. This has led to the use of Elemental Carbon as a marker for assessing human exposure to diesel exhaust, for determining the contribution of diesel engines to ambient particulate concentrations and for a surrogate for diesel particulate matter.

Hildermann et. al. , reported Elemental Carbon and Organic Carbon emissions rated for various combustion sources and determined that gasoline automobiles and oil-fired burners release significant quantities of EC [43]. Other researchers reported that the emission rate of Elemental Carbon and Organic Carbon from diesel engines varies with engine load and is not constant over the entire operating range of the engine. Recently, a study conducted by Bagely et al. (1993), characterized the physical and chemical composition of emissions from a 1988 heavy-duty diesel engine equipped with a ceramic particulate trap, and a 1991 heavy-duty diesel engine equipped with an oxidation catalytic converter [20]. The investigators determined the number and size of particles within the exhaust of the two engines tested. The results showed that, despite a substantial reduction in the weight of the total particulate matter, the total number of particles from the more advanced 1991-model engine was 15 to 35 times greater than the number of particles from the 1988 engine when both engines were operated without emission control devices. This suggests that more fine particles, a potential health concern, could be formed as a result of new technologies. Further study is needed since the extent of these findings only measured exhaust from two engines and engine technologies.

Finally, diesel vehicle exhaust particles yield an average composition (by weight) of carbon (88.3 percent), oxygen (4.9 percent), hydrogen (2.6 percent), sulfur (2.5 percent), metals (1.2percent) and nitrogen (0.5 percent) [18]. Figure 2.6 depicts this information.

Engines running under low load typically produce fewer particles with higher proportion of organic compounds associated with the available particle mass. Conversely, engines under high load typically produce more particulate matter with a lower proportion of organic compounds associated with the available particles.

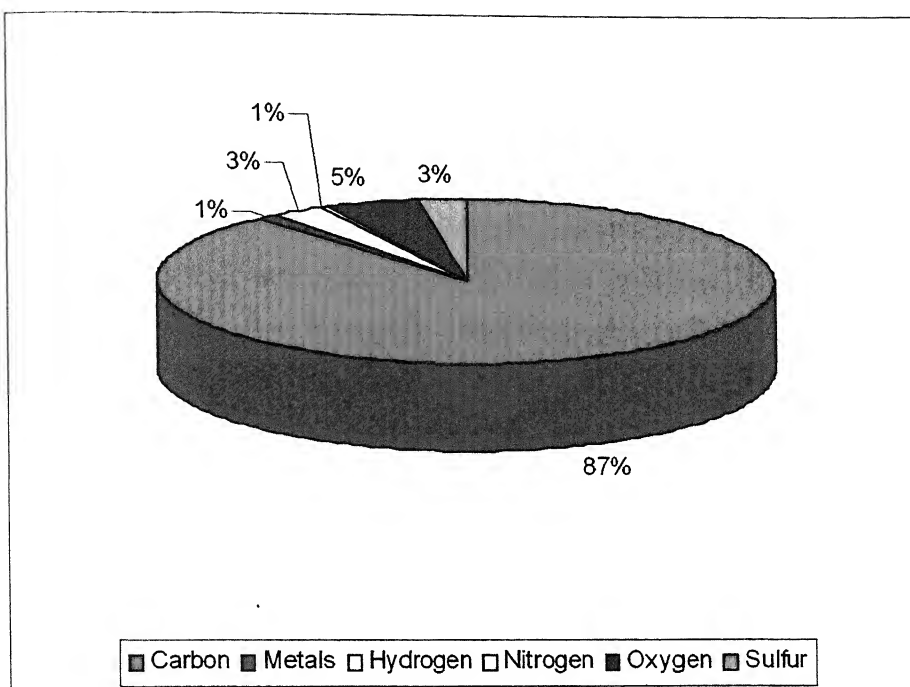


Fig 2.6: Carbon is Primary Element in Diesel Exhaust Particle [18]

Kishi et al. (1992) found that exhaust gas temperature was an important determinant for particle composition, Low exhaust gas temperatures produces particulate matter with more adsorbed soluble organics than did particulate matter produced at a high exhaust gas temperature environment [44].

Inorganic exhaust components are products of engine trace contaminants of the fuel and/or lubricant oil. The inorganic compounds associated with the particles are primarily trace fuel contaminants such as antimony, arsenic, barium, beryllium, cobalt, and strontium. These substances usually vaporize in the combustion chamber and then "plate" themselves on particles in the exhaust stream. Inorganic exhaust particles can also act as condensation-nuclei for vapour-phase components. Most research to-date has tested diesel engines on chassis and engine dynamometer facilities with either steady-state cycles or transient cycles [45]. They report that heavy-duty diesel engines following steady-state cycle release PM with 20-39% OC and 33-51% EC while heavy-duty engines following transient cycle such as the central business district cycle and hot-start federal test procedure produce PM with 30-35% OC and 30-43% EC [43]. In total it is proposed to determine Elemental and Organic carbon in diesel engine

particulates generated at various engine-operating conditions on engine dynamometer test facility.

PAH's in Diesel Engine Emissions

Over that last 10-15 years, several researchers have investigated the health effects of PAH emissions and their atmospheric transformation products. The focus for this attention arose from observed mutagenic and carcinogenic effects of this important class of compounds and their nitroderivatives. Diesel engine emissions are one of several sources of PAH and nitro-PAH emissions found in the ambient atmosphere. This section focuses on the PAH and PAH-derivatives found in diesel exhaust. In the past many studies were tried to estimate the PAH emissions from vehicles to peer the pollution predicament in urban sites [47,49,50]. Especially, the predominant hydrocarbon composition of PAH aerosols is determined by fossil fuel combustion emissions, namely, these associated with vehicular traffic [48]. PAH and PAH-derivatives present in the atmosphere are distributed between the gas and Particle phases mainly due to their liquid-phase vapor pressure [51]. They are most likely to be formed by incomplete combustion of hydrocarbons at high temperatures [52]. They are also formed from the reaction of parent hydrocarbons with nitrogen oxides in ambient air. Possible sources of PAH in diesel exhaust are unburnt PAH from the fuel, electrophilic nitration of PAH during combustion, crankcase oils, and engine or systems deposits.

A wide spectrum of gas- and particle-phase PAH and PAH-derivatives are emitted in diesel exhaust [21,53,54]. Many of the PAH that can be extracted from the exhaust particle mass are unburned fuel and/or lubricant oil components [54,55] like the fuel components naphthalene, fluorene, phenanthrene and their alkyl derivatives [56]. PAH may also be formed in the combustion chamber during the combustion of diesel fuel [57]. Methylated PAH appear to be the most abundant PAH-derivatives in diesel exhaust. Schuetzle et al. (1981) identified over 100 oxy-PAH in the moderately polar fractions of a diesel exhaust extract [58]. The extract also contained hydroxy-, ketone-, quinone-, acid anhydride-, nitro-, and carboxaldehyde-PAH-derivatives.

Kittelson et al. (1985) measured concentrations of select PAH and 1-nitropyrene in the cylinder and exhaust manifold of an operating diesel engine [52]. They observed that the PAH concentrations were higher in the cylinder than in the exhaust manifold, but the 1-nitropyrene concentrations were higher in the exhaust manifold than in the cylinder. This suggests that most of the nitro-PAH in the exhaust are probably formed during the expansion/exhaust process rather than during combustion. Honda et. al., 1984 reported that PAH emissions levels from heavy-duty diesel engine vehicles are essentially higher than those from light-duty gasoline engine cars even though there is difference in the displacement of engines [48].

Rappaport. et. al.(1980), Williams et. al.(1989), have focused their investigations on identification and quantification of particle bound PAHs from diesel-powered engines[59,60] . They reported that origin of particulate PAHs is predominantly due to unburned PAHs in the fuel, and its control techniques for PAH emission should concentrate on conventional gaseous unburned hydrocarbon reduction technique.

Westerholm and Li (1994), have reported in their studies that both diesel fuel structures and operation conditions of engine affect the chemical composition and potential biological activity of diesel emissions. It was revealed that 95% fuel PAHs in put was decomposed during the combustion process, however a major part (more than 50%) of emitted PAHs was formed from vehicle engine [61]. Generally, the PAHs content in fossil fuels does affect the formation pattern of PAHs in the combustion chamber from the exhaust of mobile vehicles. Westerholm et. al., suggested that by reducing fuel PAH contents in commercially available diesel fuel, the emissions of PAH to the environment would be reduced. Mitchell et. al., have found a good correlation between the level of Polycyclic aromatics in the diesel fuel and PAH emissions from the diesel engine. In the present study PAH's analyzed using High Performance Liquid Chromatography.

It was proposed to determine heavy molecular weight PAH's like Chrysene, Benzo (k) flouranthene, Benzo (a) pyrene, Dibenzo (a,h) anthracene, benzo (g,h,i) perylene and Indenopyrene in diesel exhaust particulates used fluorescence detector.

Chapter 3

EXPERIMENTAL SETUP AND METHODOLOGY

In order to characterize diesel engine emissions, tests were performed on Mahindra DI 2500 engine at Energy Conversion Lab, Dept. of Mech.Engg, IIT Kanpur. The study was divided into two parts, (i) Sampling (ii) Laboratory Analysis. Sampling includes collection of engine tail pipe emissions for characterization into various species. Laboratory Analysis includes analysis of the samples collected for Heavy metals, Elemental and Organic Carbon, Benzene Soluble Organic Fraction, Polycyclic Aromatic Hydrocarbons and analysis of diesel oil and fresh lubricant oil for heavy metals. This chapter presents experimental methods for both field and laboratory work.

3.1 Analyzed Diesel Engine and Dynamometer System

A Mahindra DI 2500 diesel engine was used for this study. The engine is a Four-Cylinder, Four-Stroke engine with direct-injection. Other specifications of the engine included the cubic capacity 2520 C.C., Maximum Rated Power 40 bhp@2300 RPM, Maximum Rated Torque 14 Kg-m@1400 RPM, bore and stroke 88.9 X 101.6 mm. This engine was installed and operated on an eddy-current dynamometer. The eddy-current dynamometer was equipped with a fully automatic control system and was capable of supplying maximum power and torque values in a very short time.

3.2 Sampling Procedure

The test cycle comprises of operating engine at different engine loads and speed. To characterize emissions, engine was operated at idle, 40%, 70%, 100% load conditions (Table 3.1). Samples were collected separately for analyzing Heavy Metals, Benzene Soluble Organic Fraction, Elemental and Organic Carbon and PAH's. Fig 3.1 and 3.2 represents Mahindra DI Engine and Dynamometer system.

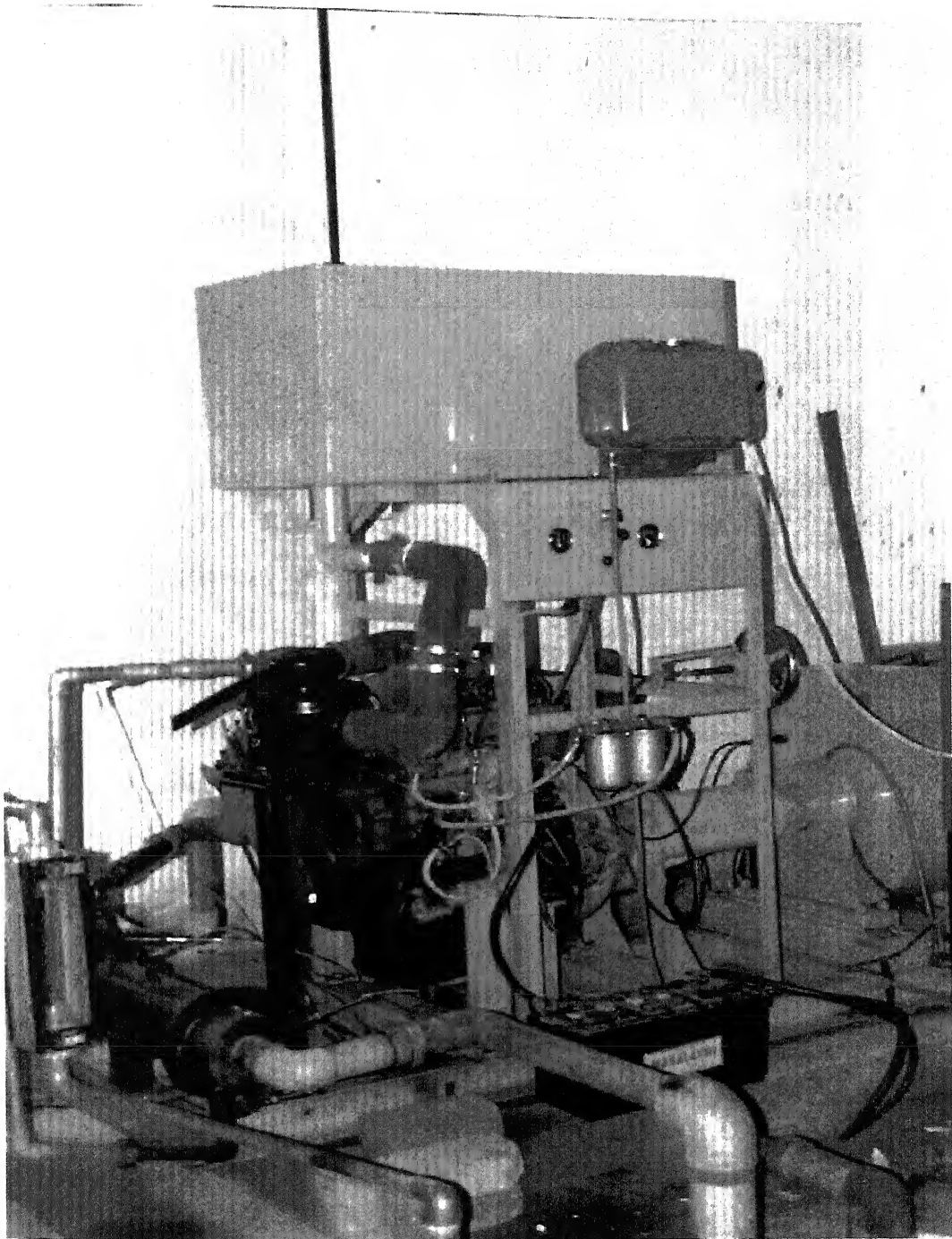


Fig 3.1: Mahindra DI Engine

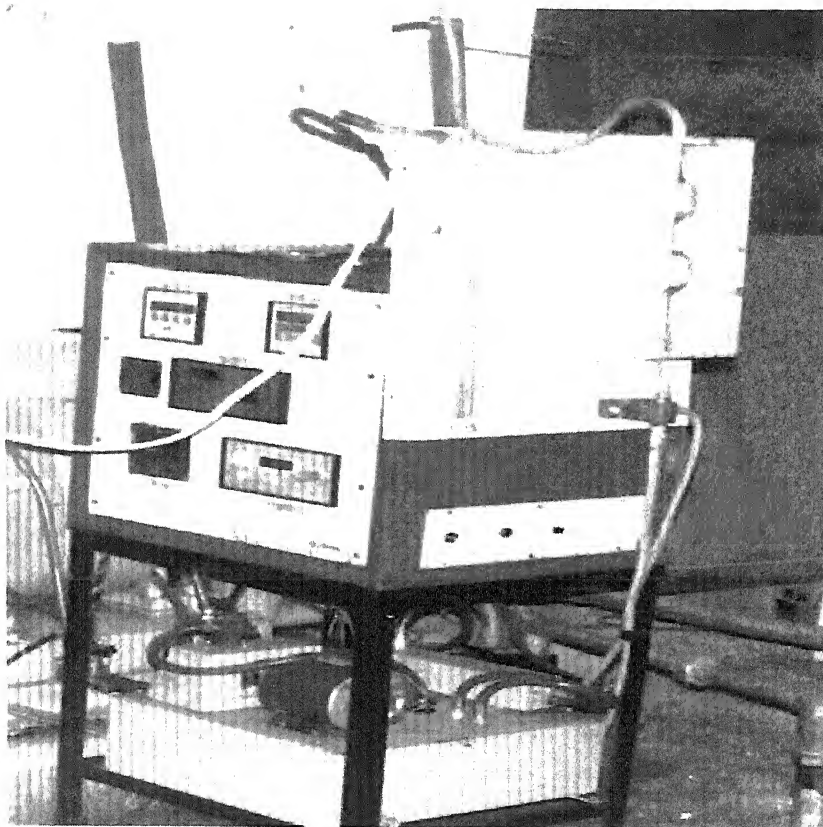


Fig 3.2: Dynamometer System of Mahindra DI Engine

Table 3.1: The Selected Operation Modes of Mahindra DI Engine

Load (%)	Speed (rpm)
Idle	2020
40	1950
70	2050
100	1400

Fig 3.3 and 3.4 illustrates tail pipe arrangement and sampling arrangement.

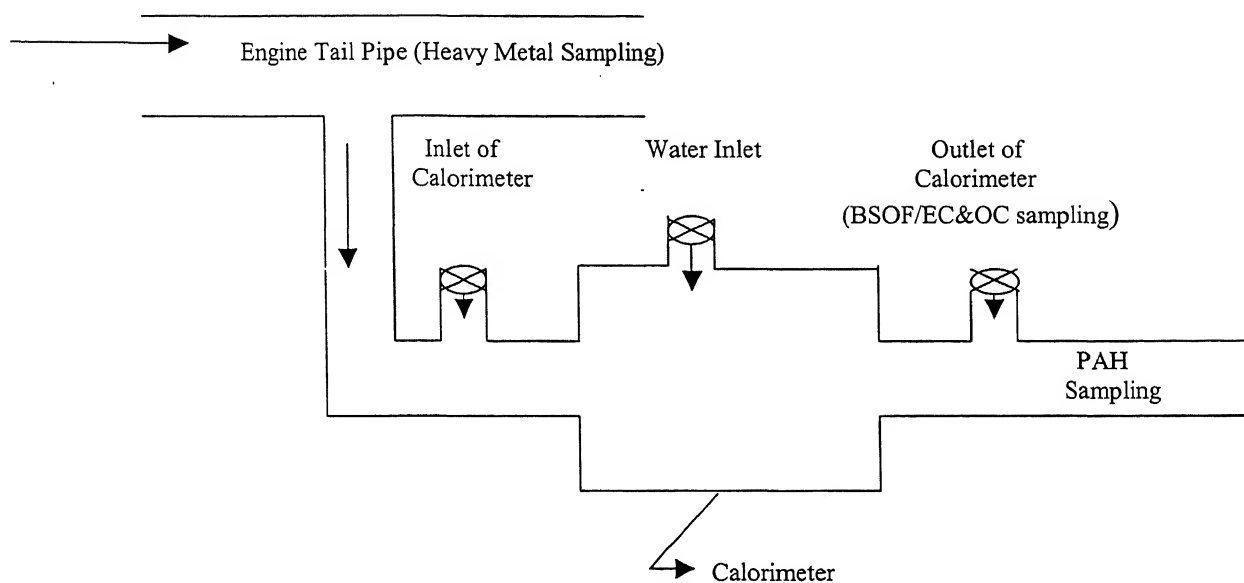


Fig 3.3: Tail Pipe Arrangement in Diesel Engine

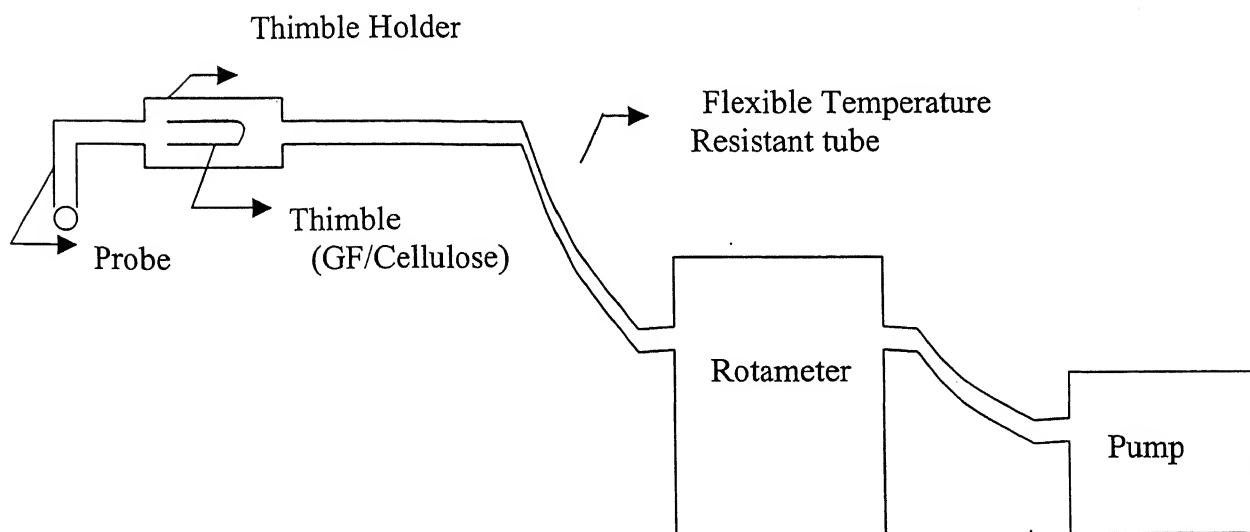


Fig 3.4: Sampling Arrangement

Particulate matter emitted from engine tail pipe was collected using a stack gas kit of (Envirotech APM 620, Delhi). The sampling arrangement consisted of nozzle, thimble holder, rotameter and a vacuum pump. Table 3.2 illustrates sampling details. The installed thimble was desiccated for 12 hrs prior to sampling and it was weighed initially on Metler Toledo balance having five-digit accuracy in grams.

Table 3.2: Details of Sampling

S.No	Samples collected for Analyzing	Thimble used	No. Of samples at each load	Duration of Sampling	Load Condition Maintained
1	Heavy Metals	GF/A (19 X 90 mm)	2	7 min (3+4)	Idle,40%,70%, 100%
2	Benzene Soluble Organic Fraction	Cellulose (19 X 90 mm)	2	30 min	Idle,40%,70%, 100%
3	Elemental & Organic Carbon	Cellulose (19 X 90 mm)	1	1 Hr	Idle,40%,70%
4	PAH's	GF/A (19 X 90 mm)	1	45 min	Idle,40%,70%

3.3 Heavy Metal Analysis Using Atomic Absorption Spectroscopy (AAS)

In view of the objectives of the research concerning characterization of the particulates, heavy metal content in particulates from Mahindra DI 2500 engine exhaust are to be analyzed. It was also decided to correlate their metal content with that of heavy metals in diesel oil and lubricant oil. AAS has been one of the most commonly used techniques for analyzing heavy metals in Particulates, diesel and lubricant oil. AAS works on the principle of absorption interaction, where atoms in the vapour-state absorb radiation at a certain wavelength that are well defined and show the characteristics of a particular atomic element. Schematic diagram of AAS has been explained in Appendix A. Heavy metals were analyzed in filter samples (collected from the tail pipe of the engine), Diesel

oil and Lubricant oil to identify the presence of the metals Fe, Mg, Cr, Ni, Pb, Zn, Ca and Ba.

3.3.1 Extraction of Samples for Heavy Metal Analysis in Particulates

In the present study sample extraction was carried out using Microwave Assisted Acid Digestion method. Samples were digested in Microwave Digestion System using EPA 3015D method [62]. This digestion procedure is used for preparing samples, which are to be analyzed on Flame Atomic Absorption Spectroscopy (FLAA). One-half of the thimble was cut into small pieces using Plastic Scissors into a Teflon vessel to which 15 ml of Conc. HNO_3 was added. The remaining half was taken in similar way into another vessel. Temperature was programmed in MDS according to the method 3015D, in which temperature of each sample was raised to 175°C in 5.5 min and remains at 175°C for another 4.5 min. After digestion, the acid from the two vessels was taken together and filtered through 0.22-micron Whatman filter paper. The filtrate was measured and diluted 3 times with Milli-Q water that are further stored in Tarson Bottles. Reference was taken as half blank thimble and 15 ml of Conc. HNO_3 . Concentrations of Fe, Mg, Cr, Ni, Pb, Zn, Ca and Ba were determined in all the above samples using Atomic Absorption Spectrophotometer (AAS) (GBC Avanta, Australia). Thimble Details are given in APPENDIX D.

3.3.2 Sample Preparation for Analyzing Heavy Metals in Diesel and Lubricant Oil

The sample preparation of Diesel and Lubricant oil was carried out using MDS. 0.5g of Diesel oil was taken in Teflon vessel to which 9 ml of Conc. HNO_3 was added. EPA 3052 method [63] was used. Temperature was programmed in MDS according to EPA 3052 method, in which temperature of each sample was raised to 180°C in 5.5 min and remains at 180°C for another 9.5 min. After digestion the acid was measured and was diluted 3 times with Milli-Q water that are further stored in Tarson Bottles. Concentrations of Fe, Mg, Cr, Ni, Pb, Zn, Ca and Ba were determined in all the above samples using Atomic Absorption Spectrophotometer (AAS) (GBC Avanta, Australia).

3.3.3 Working Standard Solutions and Calibration of Instrument

Pre-Prepared standard solutions approximately 1000 mg/L were procured (SISCO Laboratories Ltd, Mumbai). Working standard solutions of 3 different concentrations were prepared by diluting the above standard solutions with Milli-Q water. These standards were stored at 4⁰ C in Teflon Bottles. Working standards and blank are used to cover the range 0.1 to 0.8 Abs. The calibration was performed by using the blank solution to zero the instrument. The standards were then analyzed with the lowest concentration first and the blank run between standards, to ensure the baseline (zero point) has not changed. Samples are then analyzed and their absorbances were recorded. A graph of Absorbance vs. Concentration was plotted from which concentration of the sample can be read directly. Calibration curve has been explained in Appendix-A. In order to ensure the consistency and also to check the maximum possible extraction of heavy metals from the soil samples, the following procedure was adopted.

1. All the glassware and filter assembly has been subjected to acid wash and drying to avoid any contamination from previous samples
2. Blank samples were analyzed to check the possible contamination and inference from various reagents and glassware used in the analysis. It was found that the concentration of various metals in the blank sample was negligible.
3. To check concentration of heavy metals in unexposed (GF/A) thimbles used for the collection of PM from engine exhaust one half of the thimble was analyzed separately for different metals. All the filter samples were corrected for the blank concentrations of heavy metals while reporting the final concentrations.
4. Teflon vessels were thoroughly cleaned with Conc. HNO₃.
5. Prior to filtration, filter paper was cleaned using Milli-Q water and Conc. HNO₃.
6. Tarson Bottles were cleaned with 4% Conc. HNO₃ and Milli-Q water.

3.4 Estimation of Benzene Soluble Organic Fraction in Particulates

BSOF of the Particulates has been undertaken in this study. ASTM test method D 4600-87 (ASTM, 2001) [64] was used for BSOF in Particulates. This method is recommended by National Institute of Occupational Safety and Health, USA to represent the toxic

organic compounds in the particulates in filter samples. This method suggests a gravimetric determination of BSOF of the particulates.

Initially before sampling cellulose thimbles were desiccated for about 12 hrs. After sample collection thimbles were kept for desiccation for another 12 hrs and their Final weight was noted. Thimble was cut into small pieces using plastic scissors into a reagent bottle thereafter 20ml of Benzene was added to it. These reagent bottles were kept for 20 min in ultrasonic bath thereafter sample was decanted and filtered through 0.45-micron filter paper. The filtrate was collected into a 100 ml beaker. The procedure was repeated with another 10 ml of benzene in the same reagent bottle. These 100 ml beakers were covered with aluminum foil having holes and were kept in oven at 40°C for 12 to 18 hours until the sample gets dried. The initial and final weight of the beaker was measured to estimate the total mass of benzene soluble organic matter in the sample. Thimble Details are given in APPENDIX D.

In order to check the blank concentrations, blank cellulose thimble was subjected to benzene extraction as per the ASTM method. It was observed that the concentration of blank samples was found to be very less. Necessary blank corrections were made for all the samples while reporting the BSOF in particulates.

3.5 Estimation of Elemental and Organic Carbon in Particulates

The procedure performed in this study to determine particle carbon content is similar to the method described by Cachier et al. (1989) [65]. Total Carbon was analyzed using TOC analyzer (TOC-5000 (A)/5050 (A) Solid Sample Module, Shimadzu Corporation); the remaining sample was kept in oven at 340°C for 100 min to expel the organic carbon (OC) content and then fed into CE 440 Elemental Analyzer to obtain the Elemental Carbon (EC) content. The OC value was taken as the difference between TC and EC. The working principle of TOC analyzer and CE 440 Elemental Analyzer has been explained diagrammatically in Appendix A.

Initially before sampling cellulose thimbles were desiccated for about 12 hrs. After sample collection thimbles were kept for desiccation for another 12 hrs and their Final weight was noted. Thimble was cut into small pieces using Plastic scissors on to a

aluminum foil. Approximately 0.25 mg of these pieces was taken into a sample boat. This sample boat was inserted into TOC analyzer. Prior to this TOC analyzer was standardized using Glucose. The Total Carbon content was noted. The remaining sample was taken into crucible, which was kept in oven at 340°C for 100 min to expel the organic carbon (OC) content. After 100min, sample was taken and then fed into CE 440 elemental Analyzer, which gives Total Carbon content in the sample [66]. Elemental carbon was then estimated as the difference between Total Carbon and Organic carbon (assuming inorganic carbon content in sample is negligible). Thimble Details are given in APPENDIX D.

3.5.1 Calibration of Instruments

TOC analyzer-Solid module, which is used for determining Organic Carbon content, is calibrated using Glucose. 0.025 grams of glucose was weighed and was taken into sample boat, which was then inserted in TC Module. The glucose was then checked to have TC of 42 %. After calibrating instrument, sample was taken similarly in other sample boat and its TC content was noted.

CE 440 Elemental Analyzer, used to determine CHN in the sample. In case of present analysis, instrument is calibrated using OAS grade acetanilide, which was weighed more closely to the sample. The maximum sample capacity is 1000 to 3000 micrograms (in some cases up to 5000 micrograms). The samples to be analyzed were weighed in tin capsules and then injected into high temperature furnace where initial exothermic reaction occurs raising the temperature of combustion to over 1800°C (working principle and measurement technique has been explained in Appendix A)

3.6 Estimation of PAH's in Particulates from Diesel Engine Emissions

The following sequence was followed for the analysis of the PAH in Particulate samples.

1. Preparation of standards
2. Standardization of HPLC for the PAH's which were estimated.
3. Checking the span and deviation of HPLC
4. Blank tests estimation for baseline stability.

5. Sample extraction by ultrasonication
6. Sample cleanup using Silica Gel Column thereafter concentrating it using Rotary Evaporator.
7. Injection of sample into HPLC.

3.6.1 Stock Standard Solutions

Stock standard solutions were prepared using assayed reference material (Procured from Promochem Ltd., Germany) in acetonitrile. The stock solutions were stored in a 50ml glass volumetric flask and were covered with aluminum foil to protect from light. These solutions were stored at 4°C to prevent degradation or evaporation. Prior to their use stock solutions are checked for signs of degradation or evaporation, especially before preparing calibration standards.

3.6.2 Calibration Standards

Calibration standards at a minimum of five concentration levels were prepared through dilution of the stock standards with acetonitrile. These standards were prepared such that at least one concentration should be near and above the method detection limit. The remaining concentration levels correspond to the expected range found in the samples and was confirmed that they are in the working range of HPLC.

3.6.3 Extraction of samples by ultrasonication and Sample Clean Up Procedure

EPA method 8310 was adopted for the extraction of PAH compounds. Toluene was used as the solvent for extraction [67]. The thimble was cut into small pieces using plastic scissors into a reagent bottle to which 25 ml Toluene was added. These bottles were kept in ultrasonication for 45 min. The extracted sample was decanted and the procedure was repeated again with another 25 ml Toluene. The final sample thus collected was put into glass centrifuge tubes and centrifuge was done using REMI centrifuge at 700 rpm for about 30min. The supernatant was separated and was filtered through 0.45-micron Whatman filter paper. The filtrate was finally passed through a chromatographic column containing silica gel. Thimble Details are given in APPENDIX D.

3.6.4 Preparation of Silica Gel Column

About 10 grams of the activated silica gel was weighed and slurry was prepared in Toluene. This slurry was placed into the column using additional Toluene. Finally, 1 gram of anhydrous sodium sulfate was added to the top of silica gel. Prior to use, the column is rinsed with 20ml Toluene. The sample was then passed through the column and effluent was collected in a beaker. About 50ml of additional Toluene was passed through the column to ensure thorough clean up.

3.6.5 Concentration of Sample and Exchange of Solvent

The sample was concentrated to 5 ml in a rotary evaporator where the temperature was maintained about 60°C. Thereafter 2ml of acetonitrile was added and sample was concentrated to 1 ml using rotary evaporator. The procedure was repeated for another 3 ml of acetonitrile to ensure solvent exchange from toluene to acetonitrile. After concentrating, the final volume of sample was measured using Hamilton 50µl syringe. This sample was sufficiently diluted and 20 µl of this sample was then injected into HPLC for PAH analysis.

3.6.6 Analysis on High Performance Liquid Chromatography (HPLC)

Analysis of samples was done on Hitachi-Merck HPLC using Fluorescence Detector and 0.5 micron PAH column (Lichrompher) at 1 ml/min gradient flow using water and acetonitrile as mobile phase. The method, calibration curves are enclosed in Appendix-C. The following PAHs were analysed on HPLC: Chrysene, Benzo (k) Fluoranthene, Benzo (a) Pyrene, Dibenzo(a,h) Anthracene, Benzo (g,h,i) Perylene and Indenopyrene.

Chapter 4

RESULTS AND DISCUSSION

As discussed in Chapter 3, samples were collected for determination of metals, benzene soluble fraction (BSF), elemental carbon (EC) and organic carbon (OC) and polycyclic aromatic hydrocarbons (PAH's) in diesel particulate matter (DPM). The results of the study are presented under five main sections.

1. Metals in diesel particulate matter (DPM)
2. Metals in diesel and lubricating oil
3. BSF in particulates of diesel engine exhaust
4. Elemental carbon and organic carbon in particulates of diesel engine exhaust
5. PAHs in particulates of diesel engine exhaust

4.1 Metals in Diesel Particulate Matter

One of the objectives of this study was to determine metal contents in DPM; Fe, Mg, Cr, Ni, Pb, Zn, Ca, Ba and Cd were measured in DPM under various engine load conditions (Tables 4.1 and 4.2). The experimental study showed that concentrations of Fe, Mg, Ca (crust elements) were much higher than those of the Cr, Ni, Pb, Zn, Ba and Cd (anthropogenic elements). Figures 4.1 and 4.2 present the variation of concentration of crust and anthropogenic elements in DPM with respect to engine load. The metal concentrations of this study have been compared with the results of Wang et al. (2003) [38] (Figure 4.3).

Table 4.1: Metal Concentrations in Particulates of Diesel Engine Exhaust

S.No	Metal	Metal Concentration ($\mu\text{g}/\text{m}^3$)				
		Engine Load				Wang et al. (2003) [38] (100% load)
		Idle	40%	70%	100%	
1	Fe	258	221.2	195.6	172.3	543
2	Mg	125	112.8	95.4	86.5	138
3	Cr	59.2	46.3	35.2	31.8	88.6
4	Ni	42.1	36.0	32.2	24.9	51.1
5	Pb	35.2	28.1	24.6	18.3	40.6
6	Zn	85.6	76.3	72.5	68.1	111
7	Ca	936	845	823	815	831
8	Ba	16.1	14.9	13.5	12.6	23.1
9	Cd	ND	ND	ND	ND	10.7

Table 4.2 Metal Concentrations in Particulates of Diesel Engine Exhaust (mg per gram of particulate emission)

S.No	Metal	Metal Concentration (mg/g) under various Engine Load Conditions			
		Idle	40%	70%	100%
1	Fe	5.160	2.457	1.910	1.265
2	Mg	2.500	1.253	0.931	0.635
3	Cr	1.184	0.514	0.343	0.233
4	Ni	0.842	0.400	0.314	0.182
5	Pb	0.704	0.312	0.240	0.134
6	Zn	1.712	0.847	0.708	0.500
7	Ca	18.72	9.388	8.038	5.984
8	Ba	0.322	0.165	0.131	0.092
9	Cd	ND	ND	ND	ND

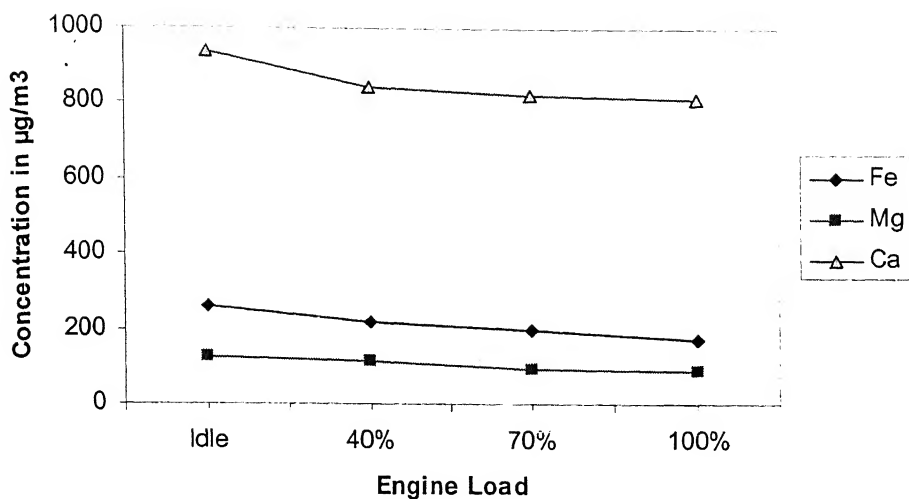


Fig 4.1: Variation of Concentration of Fe, Mg, Ca (crust elements) with Engine Load

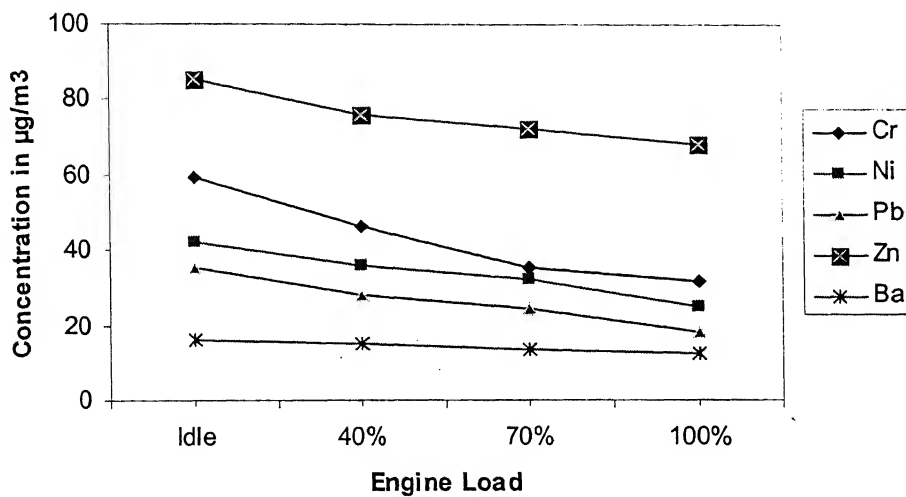


Fig 4.2: Variation of Concentration of Cr, Ni, Pb, Zn, Ba (anthropogenic elements) with Engine Load

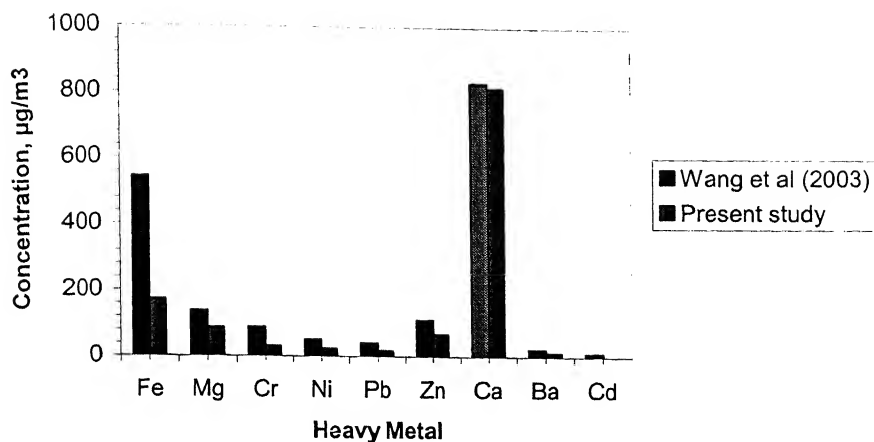


Fig 4.3: Metal Concentration in Particulates

It is evident from Figures 4.1 and 4.2 that generally the metal levels in DPM decrease with increase in load. The efficiency of diesel engine improves with load typically up to 90 percent of load. In other words, diesel input per unit of power derived decrease and that is reflected in reduced emission of metals with load. Although the metal levels are generally lower (by a factor of 1.5-3) in this study compared to those reported by Wang et al (2003) [38], the relative emission trend from one metal to another is similar (Figure 4.3). Wang et al (2003) [38] have reported that the most of the emissions of metal in DPM is from metals present in the diesel, therefore, it is desirable to compare metal contents in emission with metals present in diesel.

4.2 Heavy Metal Concentration In Diesel and Lubricating Oil

Fe, Mg, Cr, Ni, Zn, Pb, Ca, Ba, and Cd were measured in diesel and lubricating oil. Figures 4.4 (crust metals) - 4.5 (anthropogenic metal) present the concentration of metals in diesel. The results of the present study were compared in Table 4.2 with studies of Wang et al, (2003) and Palus et al, (1998) [38, 52].

Table 4.2: Heavy Metal Concentration in Diesel and Lubricating Oil

S.No	Metal	Heavy metal concentration in $\mu\text{g/g}$			
		Diesel		Lubricating Oil	
		Present study	Wang et.al (2003) [38]	Present Study	Palus et al. (1998) [52]
1	Fe	155	27.8	15	1.29
2	Mg	47	7.12	40	16.01
3	Cr	28	4.4	ND	Not reported
4	Ni	25	2.61	ND	Not reported
5	Pb	35	2.04	ND	2.80
6	Zn	29	5.63	878	2116.50
7	Ca	139	41.2	4129	5083.86
8	Ba	3.2	1.12	ND	27.31
9	Cd	2.8	0.525	0.2	0.15

Note: Cr, Ni, Cd and Pb were below detection limit and were taken as half of the detection limit.

It was found that concentration of Fe, Ca, Mg are dominant among the crust elements, in case of lubricating oil Zn, Ca are dominant.

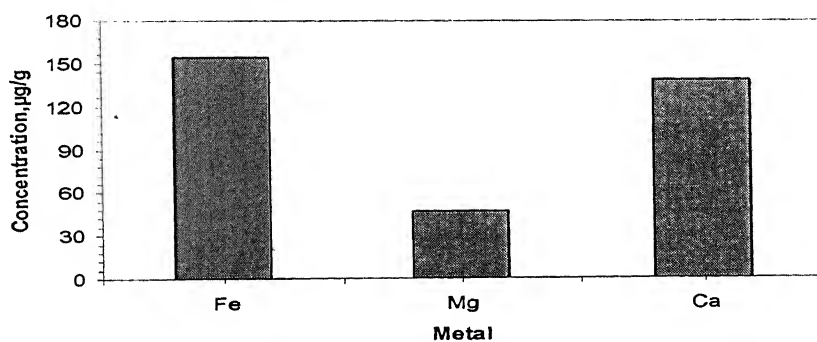


Fig 4.4: Crust Elements Concentrations in Diesel

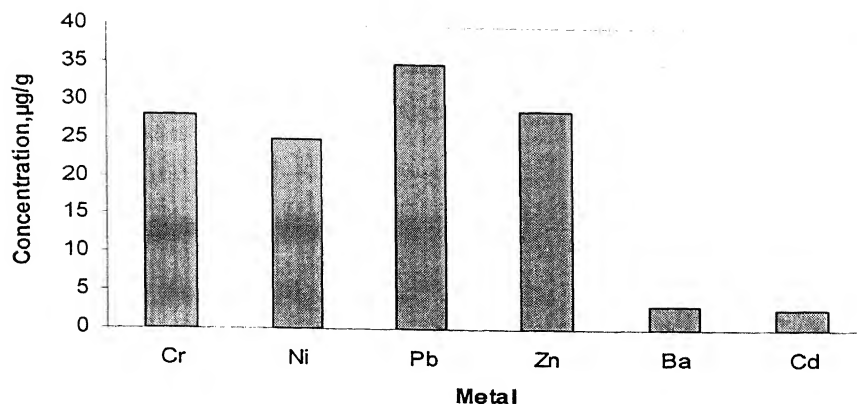


Fig 4.5: Anthropogenic Elements Concentrations in Diesel

These figures support the fact that metal content in diesel can possibly play an important role in the emission of metals in the DPM. It is evident from Table 4.2 that upon comparison with the other studies [38,52] crust and anthropogenic metal concentrations are higher in this study.

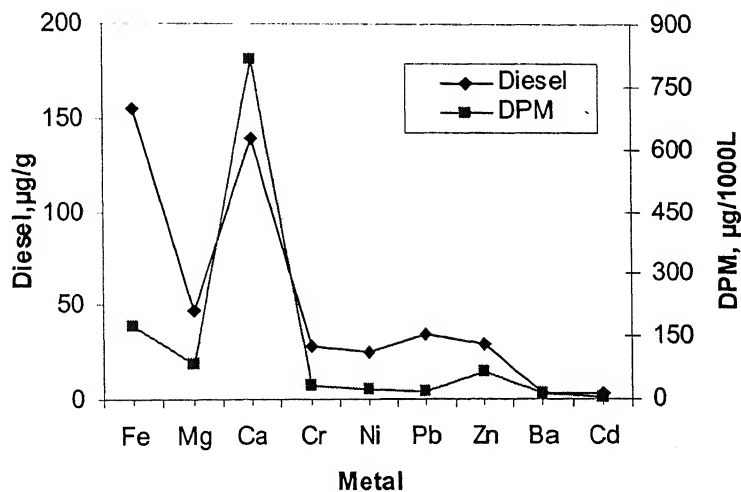


Fig 4.6: Comparision of Metal Content in Diesel with Metal Content in DPM

An attempt has been made to examine the influence of metal content in diesel on metal content in DPM (Figure 4.6). The correlation coefficient between metal contents of diesel and in DPM was found to be 0.73. Although it is not possible to estimate the emission of

metals per unit consumption of diesel (as specific diesel consumption was not measured under various load conditions), the high correlation and Figure 4.6 suggest that concentrations of metals in DPM are mostly dependent on metals concentration in diesel.

4.3 Benzene Soluble Fraction (BSF) in DPM

BSF has been taken as indicator of organic fraction of particulates which represents a reasonable measure of toxic compounds [42]. Results of BSF in DPM are presented in Table 4.3 and Figure 4.6. It can be observed that at idling condition BSF was about 67% and reduces with increase in engine load. This can be explained by the fact that at idle condition the diesel and lubricating oil undergoes partial combustion (pyrolysis) due to low temperature conditions prevailing in the combustion chamber. This leads to higher unburnt hydrocarbon species emissions, which are detected as BSF. The results of present study were compared with the work of Ning et al. (2004) [59] (Table 4.3) who examined the soluble organic fraction using soxhlet extraction.

Table 4.3: Benzene Soluble Organic Fraction in Particulates (% w/w)

Engine Load Condition	BSF (% w/w)	SOF (%w/w) Ning et al. (2004) [59]
Idle	66	>100
40%	52	92
70%	28	57
100%	24	22

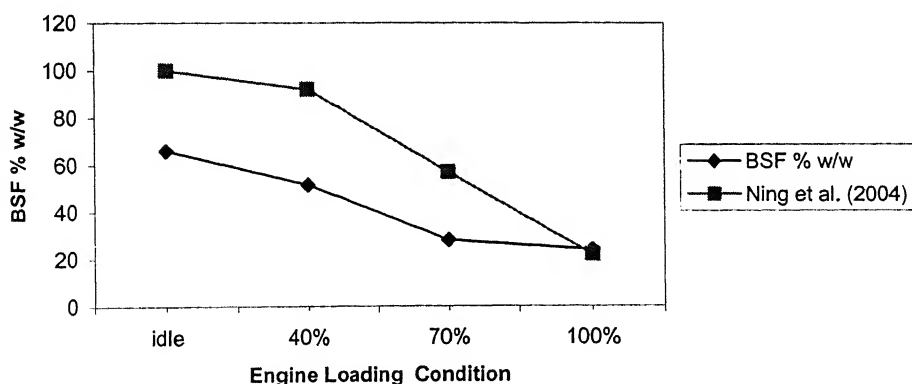


Fig 4.6: Variation of BSF with Engine Load

It can be observed that pattern of variations in both the studies are comparable. The values in the present study are less than Ning et al. (2004) [59] due to difference in particulate concentrations and engines studied. The results indicated that at low load conditions, the main component of the diesel particulate was SOF, which had a proportion of up to 66 % by weight. As the engine load was increased to 100 %, the proportion of soluble organic fraction decreased rapidly, dropping to 24 % at rated operating condition.

4.4 Elemental Carbon and Organic Carbon in DPM

As per the methodology mentioned in Chapter 3, the particulate samples were analyzed on TOC Analyzer and CE 440 Analyzer for OC and EC determination. It was assumed that inorganic carbon (other than elemental carbon) content was negligible. The results of total carbon, elemental carbon and organic carbon are shown in Table 4.4. It can be seen that, at idling condition total carbon was about 60% by weight, which gradually increased to 74.9 % at 70 % loading condition. The EC also showed the same trend. The trend of OC was opposite, OC % was 35% at idle condition, which is maximum, and it dropped down to 25 % at 70 % load which is also reflected in BSF measurements; this is an independent test that OC emission decrease with increase in load but there is a greater chances of forming EC with increase in load. Fig 4.7 shows variation of EC and OC with engine loading conditions. Although Crocker et al., (2004) [38] have reported EC and OC percentages in DPM at various engines loads, the load conditions in their study and our study are not the same and cannot be compared directly. However, in two studies, the trend in OC and EC (in DPM) with increase in engine load is the same; OC emission decrease with increase in load and EC increase with increase in load. The EC and OC at the nearest load conditions of the two studies are compared in Figure 4.8.

Table 4.4: Elemental Carbon and Organic Carbon in Particulates

Engine Loading Condition	Total Carbon, TC%	Elemental Carbon, EC%	Organic Carbon, OC%
Idle	60	25	35
40%	64	38	26
70%	74	48	25

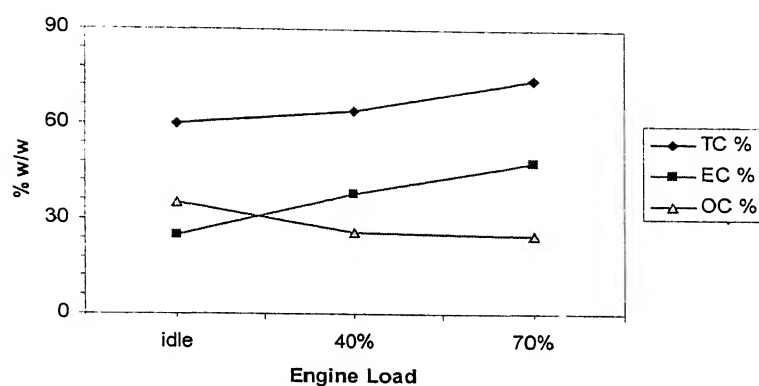


Fig 4.7: Variation of EC and OC with Engine Loading Condition

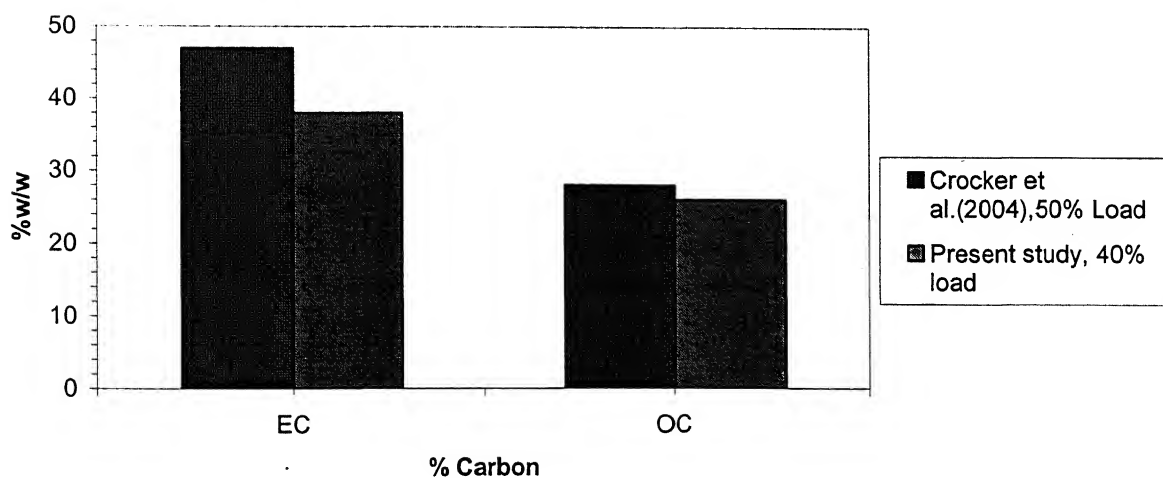


Fig 4.8: Comparison of EC and OC values

4.5 PAHs in Particulates

PAH concentrations in the particulates of Mahindra DI engine were affected by engine loads. The particulates collected in thimbles at different engine loads were analyzed for 6 PAHs namely chrysene, benzo(k)flouranthene ,benzo(a) Pyrene, dienzo(a,h) anthracene, benzo(g,h,i) perylene and indenopyrene. The indenopyrene was not detected in any of the particulates samples. Initially a recovery study has been carried out by preparing matrix of the above 6 PAHs. Table 4.5 gives details of recoveries obtained for all 6 PAHs under study. It was found that for most of the PAHs recoveries were above 65 % except for benzo(a)pyrene, dibenzo(a,h)anthracene whose recoveries were 46% and 22% respectively. It may be noted that only one sample of PAHs was taken and internal standards were not used. In view of the fact that only one sample was taken and recoveries for two PAHs were low, results must be interpreted/reported with caution and say data reliability may be low. The concentrations of the PAHs are reported in Table 4.6.

Table 4.5: PAHs Recovery Study

PAH COMPOUND	% Recovery
CHRYSENE	69
BENZO (k) FLOURANTHENE	61
BENZO (a) PYRENE	46
DIBENZO (a,h) ANTHRACENE	22
BENZO (g,h,i) PERYLENE	85
INDENOPYRENE	64

Table 4.6: Concentration of PAHs in Particulates

PAH COMPOUND	PAH concentration in $\mu\text{g/g}$ at Various Engine Load		
	Idle	40%	70%
CHRYSENE	1.259	187.81	75.300
BENZO (k) FLOURANTHENE	1.282	165.63	57.022
BENZO (a) PYRENE	0.018	3.802	1.483
DIBENZO (a,h) ANTHRACENE	0.029	3.572	1.184
BENZO (g,h,i) PERYLENE	ND	0.406	0.151

Note: low reliability in data.

The concentration of chrysene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i) perylene increased with increase in load from idle to 40% and decreased thereafter for 70% concentration load. The evaluation of the PAHs for 100% load could not be carried out because of instrumental breakdown.

4.6 Particulate Composition

As stated in Chapter 2, the particles emitted from diesel engines are mainly aggregates of spherical carbon particles coated with organic and inorganic substances with the composition of the particles being predominantly, 80 to 90 percent, organic and inorganic carbon. Figure 4.10 - 4.13 shows particulate composition at various engine load conditions along with the composition given by Volkswagen et al., (1989) [18]. It can be seen that the broad composition of the particulate remains the same with load and also when compared to the study of Volkswagen (1989). But a closer examination suggests that the composition may dramatically changed between OC and EC with variable load including idle conditions. The particle composition of diesel exhaust emissions can vary greatly depending on the engine type, engine speed and load, fuel composition, lubricating oil type and emission control technology [1]. Therefore, there is a need to account for varying DPM composition while estimating (i) the source profile, (ii) emission inventory and (iii) health implications of DPM.

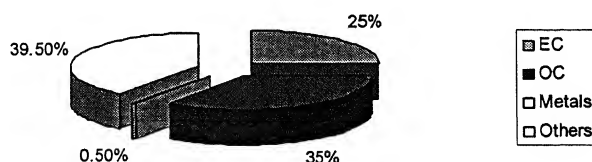


Fig 4.10: Particulate Composition at Idle Condition



Fig 4.11: Particulate Composition at 40 % Load

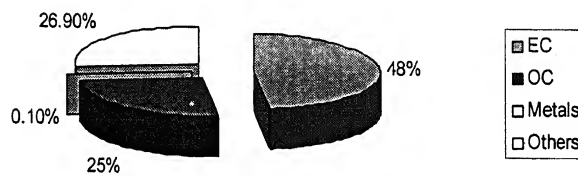


Fig 4.12: Particulate Composition at 70% Load

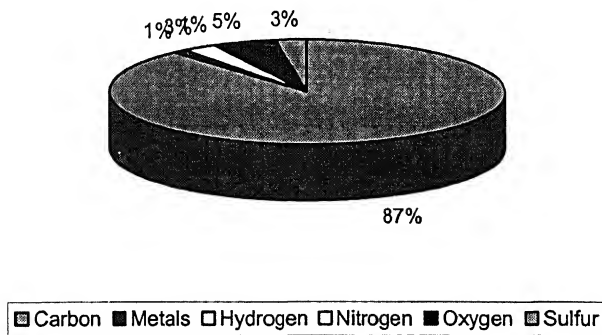


Fig 4.13: Particulate Composition given by Volkswagen (1989) [18]

Chapter 5

CONCLUSIONS AND SCOPE FOR FUTURE WORK

5.1 Conclusions

The experimental investigation on the particulate matter emitted by direct diesel engine contains significant amounts of heavy metals, crust metals, benzene soluble organic fraction and PAHs. Most of the metals present in the particulate matter originate from wear of various vital engine parts. Lead however is primarily contributed by diesel. The concentrations of all heavy and crust metals (except Pb) decrease with increase in engine load. Although the emission of anthropogenic elements from diesel engine exhaust was much less than that of crust elements, the contribution of the former to the ambient environment could be much more significant than the later. It is evident from the experimental investigations that the metal content in diesel and lubricating oils significantly affect metal emissions from the engine and their contribution from fuel and lubricating oil may be different for different countries. BSOF is a good indicator of presence of toxic organic compounds. BSOF in particulates of diesel engine exhaust varies from 27 to 70% for different engine loads. This suggests that apart from metallic emissions, diesel engines also contribute to toxic organic compounds specifically neutral and aromatic organics. Total carbon analysis reveals that the diesel particulates may contain upto 70 % carbon. Several PAHs are adsorbed by the particulates, which may have harmful effects on human health. Insignificant amount of PAHs are emitted at idling conditions. The PAH emissions increases with increase in load and further reduces towards full load conditions.

5.2 Scope for Future Work

This study can be further extended to experimentally evaluate the contribution of different sources (such as diesel, lubricating oil, wear metals etc.) to the emission of metals in the exhaust of diesel engine under different loads. This would give information about the sources of various metals in the exhaust, which can finally be controlled at the source. The above research can be continued in order to estimate emission rates of metal contents in engine exhaust and consumption rates of diesel fuel. PAH emissions from diesel engines can be correlated with their content in diesel and therefore one can regulate these emissions by modifying fuel composition rather than engine modifications. Comprehensive study may be taken up to evaluate the health effects of these heavy metals, BSOFs and PAHs on human health.

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Appendix-A: Details of Instruments Used

A.1 Atomic Absorption Spectroscopy

Atomic Absorption Spectroscopy works on the principle of absorption interaction, where atoms in the vapour state absorb radiation at a certain wavelength that are well defined and show the characteristics of a particular atomic element. In this process, the source of radiation projects a beam of a specific wavelength through a pure flame (air-acetylene/nitrous oxide - acetylene) on to a sensor and the amount of radiation arriving at the photo sensor is recorded. The fluid sample is introduced into the flame and vaporized. The amount of radiation arriving at the photo sensor is reduced in proportion to the quantity of the specific element present in the sample.

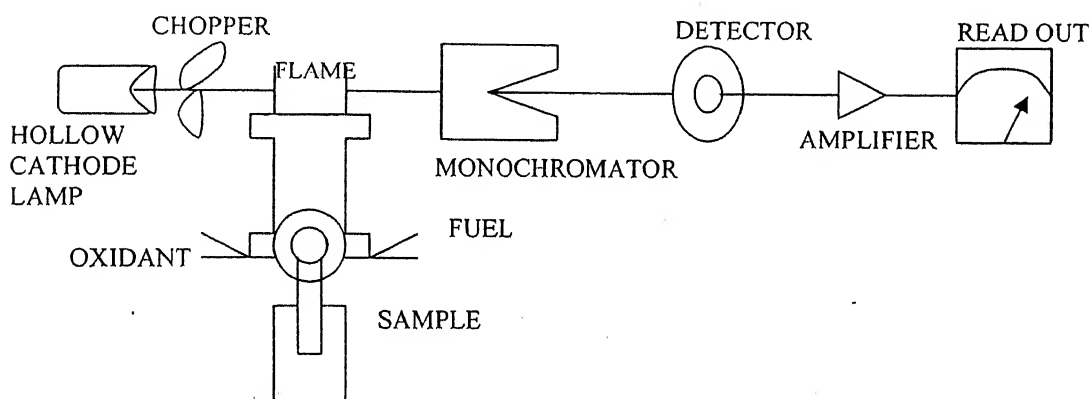


Fig A.1.1: Schematic Diagram for Atomic Absorption Spectroscopy



Fig A.1.2: GBA Avanta Atomic Absorption Spectroscopy

Calibration Curve:

This is the most common method where interference effects are known to be absent. Usually at least three standards and a blank are used to cover the range 0.1 to 0.8 Abs. The calibration is performed by using the blank solution to zero the instrument. The standards are then analyzed with the lowest concentration first, and the blank run between standards, to ensure the baseline has not changed. Samples are then analyzed and their absorbances recorded. A graph of Absorbance vs. Concentration is plotted and a typical curve is shown in Figure A.3, where A1, A2, A3 are absorbances of Standard 1, 2, 3 and C1, C2, C3 are concentrations of Standards 1, 2, 3. As and Cs represents absorbance and Concentration of Sample

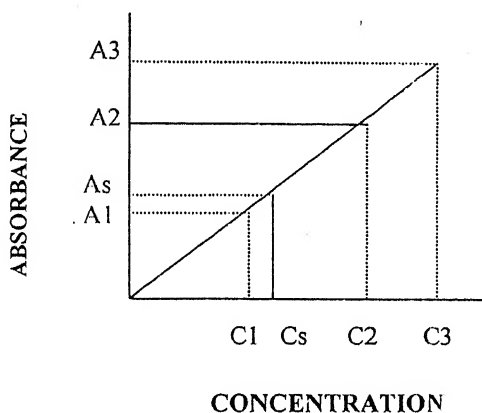


Fig A.1.3: Calibration Curve

A.2 Microwave Digestion System (MDS) -MILESTONE ETHOS E

Fundamentals of Microwave Digestion:

Conventional wet-sample preparation methods for the decomposition of solid samples are usually carried out in vessels containing the sample and a large volume of decomposition reagent(s), typically 15 to 100 mL. This mixture is heated for long periods of time using a hot plate, heating mantle, or oven. Heating is terminated when the analyst decides that the decomposition of the sample is sufficiently complete. This type of open-vessel digestion has many drawbacks, which include the use of large volumes (and multiple additions) of reagents, a large potential for contamination of the sample by materials and laboratory environment, and the exposure of the analyst and the laboratory to corrosive fumes.

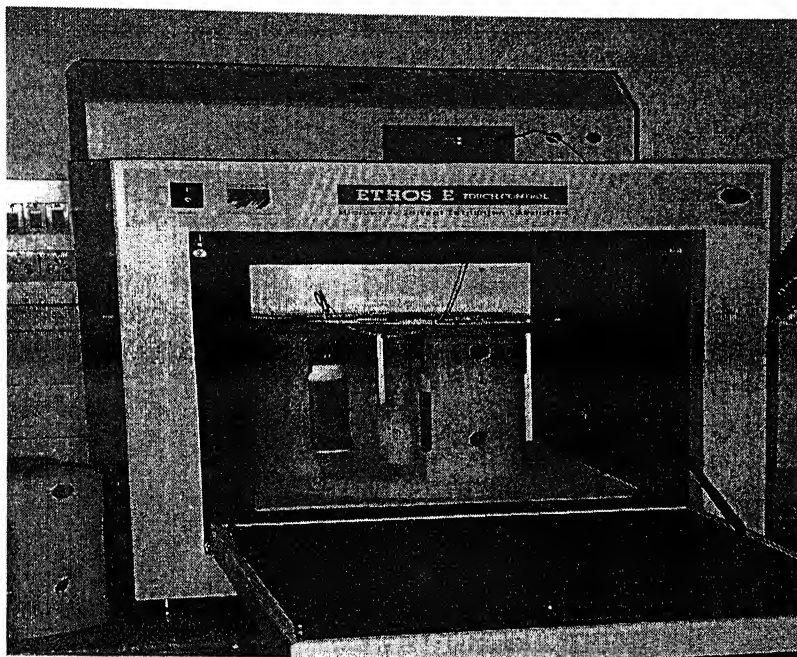


Fig A.2: Milestone ETHOS E Microwave Digestion System

Closed-vessel microwave decomposition uses significantly different technology and fundamentally unique principles to accomplish sample decomposition. Decomposition of most solid samples can be achieved using near stoichiometric quantities of reagents, typically 10 mL, and can usually be completed in 10 to 15 minutes. This decrease in sample preparation time can be attributed to the closed vessels and the rapid heating of the sample mixture. The higher temperatures achieved in the closed system give microwave digestion a kinetic advantage over hot plate digestion.

A.3 Total Organic Carbon Analyzer (TOC)

The DRI thermal/optical carbon analyzer is based on the preferential oxidation of organic carbon (OC) and elemental carbon (EC) compounds at different temperatures. It relies on the fact that organic compounds can be volatilized from the sample deposit in a helium (He) atmosphere at low temperatures, while elemental carbon is not oxidized and removed. The analyzer operates by: 1) liberating carbon compounds under different temperature and oxidation environments from a small sample punch (normally 0.536 cm²) taken from a quartz fiber filter; 2) converting these compounds to carbon dioxide (CO₂) by passing the volatilized compounds through an oxidizer (heated manganese

dioxide, MnO_2); 3) reduction of CO_2 to methane (CH_4) by passing the flow through a methanator (hydrogen-enriched nickel catalyst); and 4) quantification of CH_4 equivalents by a flame ionization detector (FID).

The principal function of the optical (laser reflectance) component of the analyzer is correction for pyrolysis of organic carbon compounds to elemental carbon. Without this correction, the organic carbon fraction of the sample would be underestimated and the elemental carbon fraction would be overestimated by including some pyrolyzed organic carbon. The correction for pyrolysis is made by continuously monitoring the filter reflectance (via a helium-neon laser and a photodetector) throughout an analysis cycle. This reflectance, largely dominated by the presence of light absorbing elemental carbon, decreases as pyrolysis takes place and increases as light absorbing carbon is liberated during the latter part of the analysis. By monitoring the reflectance, the portion of the elemental carbon peak corresponding to pyrolyzed organic carbon can be accurately assigned to the organic fraction. The correction for pyrolytic conversion of organic to elemental carbon is essential for an unbiased measurement of both carbon fractions, as discussed in Johnson et al. (1981).

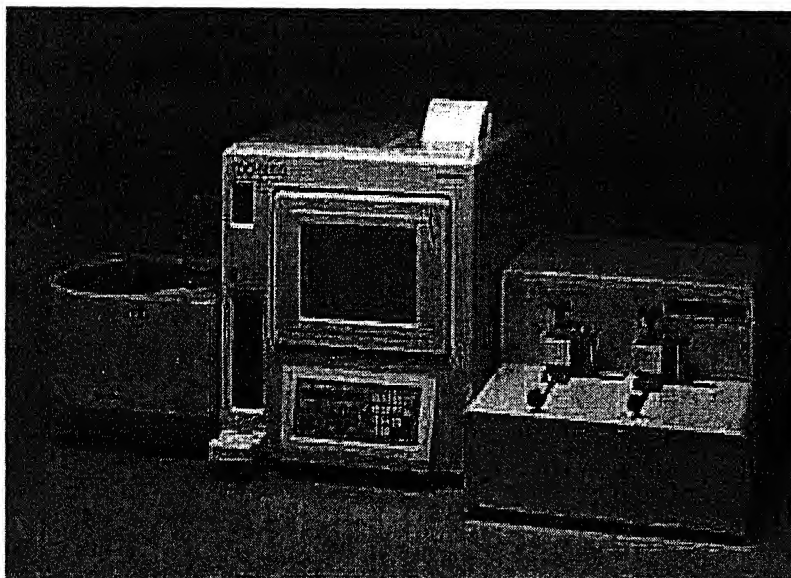


Fig A.3: TOC 5000(A)/ 5050 (A)

A.4 CE440 (CHN /O/S) ELEMENTAL ANALYZER

Theory of Operation:

The samples to be analyzed are weighed into disposable tin or aluminum capsules. The sample is injected into a high temperature furnace and combusted in pure oxygen under static conditions. At the end of the combustion period, a dynamic burst of oxygen is added to ensure total combustion of all inorganic and organic substances. If tin capsules are used for the sample container, an initial exothermic reaction occurs raising the temperature of combustion to over 1800°C. The resulting combustion products pass through specialized reagents to produce from the elemental carbon, hydrogen, and nitrogen; carbon dioxide (CO₂), water (H₂O) and nitrogen (N₂) and N oxides. These reagents also remove all other interferences including halogens, sulfur, and phosphorous.

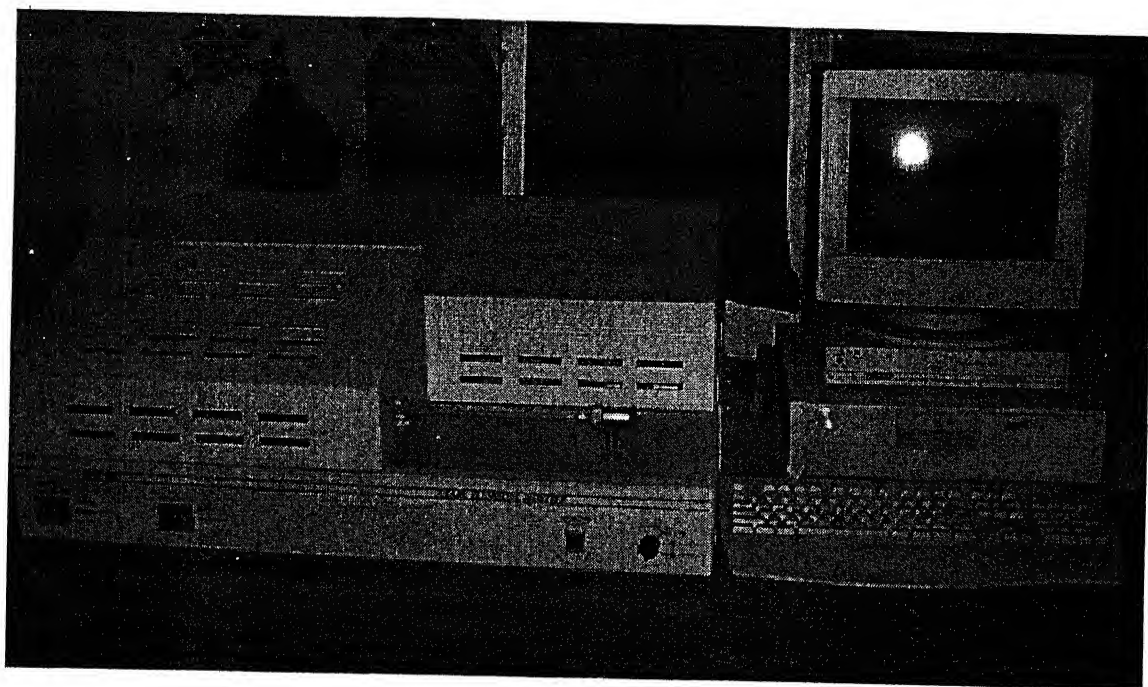


Fig A.4 :CE 440 Elemental analyzer

The gases are then passed over copper to scrub excess oxygen and reduce oxides of nitrogen to elemental nitrogen. After scrubbing, the gases enter a mixing volume chamber to ensure a homogeneous mixture at constant temperature and pressure. The mixture then passes through a series of high-precision thermal conductivity detectors, each containing a pair of thermal conductivity cells. Between the first two cells

is a water trap. The differential signal between the cells is proportional to the water concentration, which is a function of the amount of hydrogen in the original sample. Between the next two cells is a carbon dioxide trap for measuring carbon. Finally, nitrogen is measured against a helium reference. Sulfur is measured separately, as sulfur dioxide, by replacing the combustion and reduction reagents. Oxygen is also measured separately by pyrolysis in the presence of platinized carbon. The oxygen is finally measured as carbon dioxide. Both analyses are easily carried out and require a simple change of reagent tubes. In this way the analysis of either sulfur or oxygen is not compromised by trying to determine several elements at the same time.

A.5 High Performance Liquid Chromatography

High performance liquid chromatography (HPLC) is a separation technique utilizing differences in distribution of compounds to two phases, called stationary phase and mobile phase. The stationary phase designates a thin layer created on the surface of fine particles and the mobile phase designates the liquid flowing over the particles. Under a certain dynamic condition, each component in a sample has a different distribution equilibrium depending on solubility in the phases and/or molecular size. As a result, the components move at different speeds over the stationary phase and are thereby separated from each other. This is the principle behind HPLC. The column is a stainless steel (or resin) tube, which is packed with spherical solid particles. Mobile phase is constantly fed into the column inlet at a constant rate by a liquid pump. A sample is injected from a sample injector, located near the column inlet. The injected sample enters the column with the mobile phase and the components in the sample migrate through it, passing between the stationary and mobile phases. Compounds move in the column only when in the mobile phase. Compounds that tend to be distributed in the mobile phase therefore migrate faster through the column while compounds that tend to be distributed in the stationary phase migrate slower. In this way, each component is separated on the column and sequentially elutes from the outlet. Each compound eluting from the column is detected by a detector connected to the outlet of the column. There are two detectors: UV detector and Fluorescence detector.



Fig A.5.1: High Performance Liquid Chromatography

When the separation process is monitored by the recorder starting at the time the sample is injected, a graph is obtained. This graph is called a chromatogram. The time required for a compound to elute (called retention time) and the relationship between compound concentration (amount) and peak area depend on the characteristics of the compound. Retention time is therefore used as an index for qualitative determination and peak surface area (or height) as an index for quantitative determination. The retention time of the target compounds and the concentration for each unit of peak area are based on data obtained in advance by analyzing a sample with known quantities of the reference standards. Normally, the reference standards are highly purified target compounds. A HPLC system is basically composed of 1) a pump, 2) an injector, 3) a column, 4) a column oven and 5) detector, as shown in Fig.A.5.2

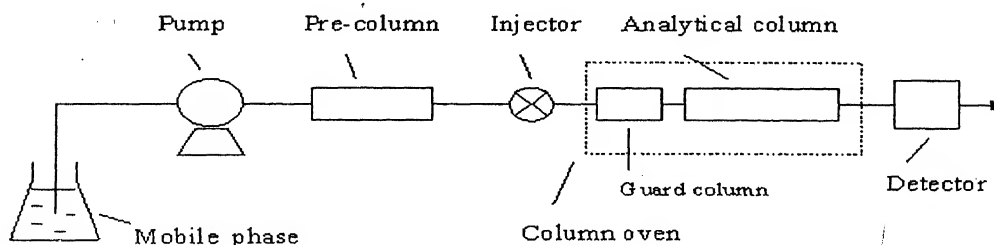


Fig.A.5.2 HPLC System

The UV detector, where UV stands for ultraviolet radiation, is the detector, which is most generally useful. It is used to detect compounds with strong UV absorption, e g aromatic and especially Polycyclic Aromatic Compounds. There are different types of UV detectors, e.g, diode array detectors and scanning UV detectors, the latter recording an entire spectrum. A fluorescence detector is used for fluorescent compounds, or compounds made fluorescent by derivatization. It can be up to 1000 times more sensitive than the UV detector. Its high specificity also results in less interference from the background (i.e, from the solvent or from impurities). A common application within environmental chemistry is the detection of Polycyclic Aromatic Hydrocarbons (PAHs).

Appendix B: USEPA Recommended Cleaning Procedure For Cleaning Vessels

The procedure is described in the US EPA approved method 3052 for total digestion of environmental samples.

1. Store vessels and covers overnight in 1:1 sub-boiled HCl at 80-95⁰C
2. Rinse with bi-distilled water
3. Store vessels and covers overnight in 1:1 sub-boiled HNO₃ at a 80-95⁰C
4. Rinse with bi-distilled water
5. Store vessels and covers overnight in bi-distilled water
6. Allow vessels and covers to dry in a particle and fume-free environment prior to use.

Appendix C: Standardization of HPLC

Initially Matrix of selected 6 PAH compounds namely, Chrysene, Benzo (k) Flouranthene, Benzo (a) pyrene, Dibenzo (a,h) anthracene, Benzo (g,h,l) Perylene and Indenopyrene was made. Following Table C-1 gives the concentration of individual compounds and different dilutions of this matrix was prepared for calibrating instrument. Calibration Curves are shown in Fig C-1 to C-9 and method is enclosed

Table C-1: Concentrations of Standard matrix

PAH compound	Original Concentration in $\mu\text{g/l}$	Vol taken for preparing matrix in μL
Chrysene	14000	700
Benzo(K) flouranthene	6000	1500
Benazo(a) pyrene	2000	850
Dibenzo (a,h) anthracene	4000	120
Benzo (g,h,l) Perylene	11000	340
Indenopyrene	3000	1200

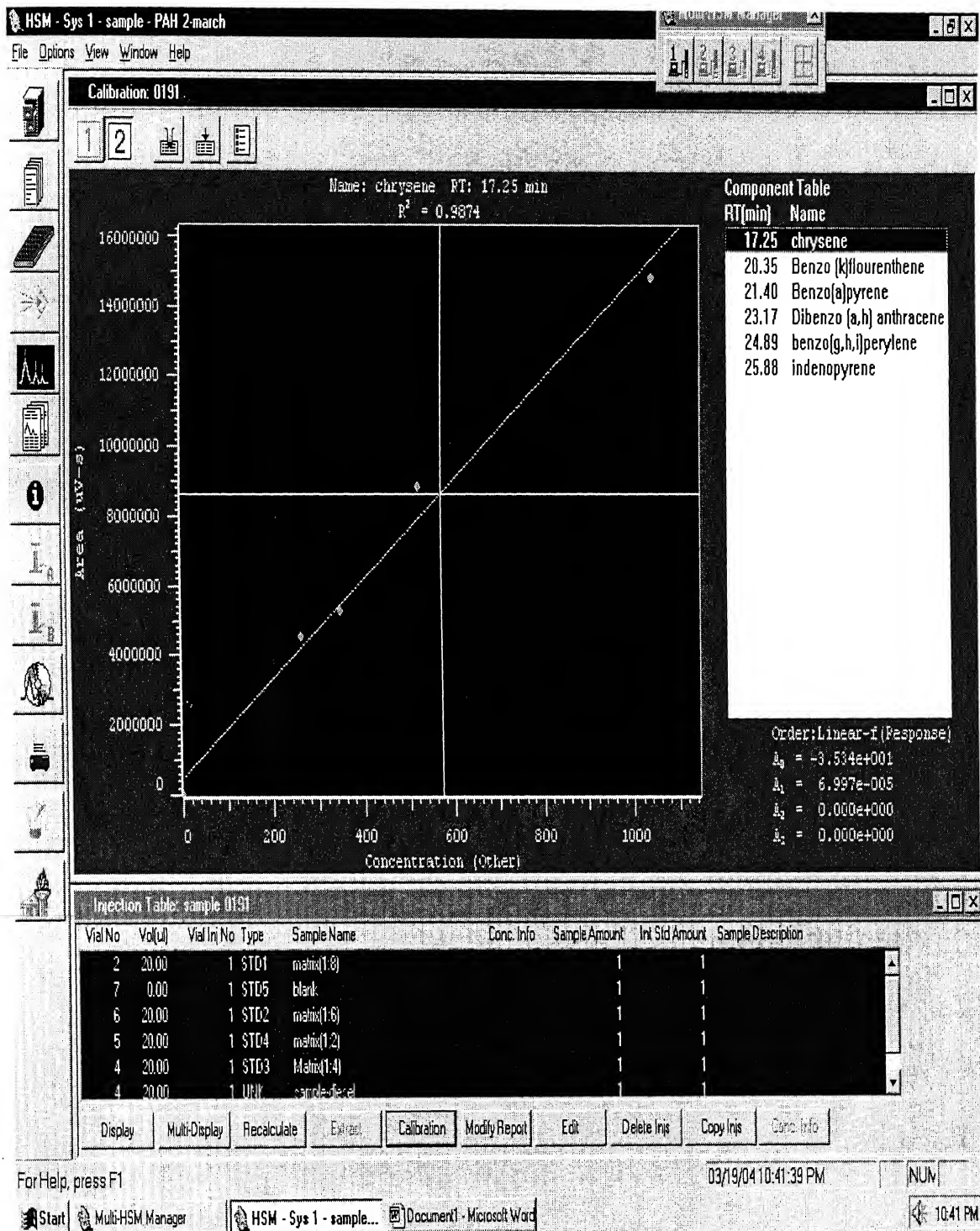


Fig:C-1: Calibration Curve of Chrysene

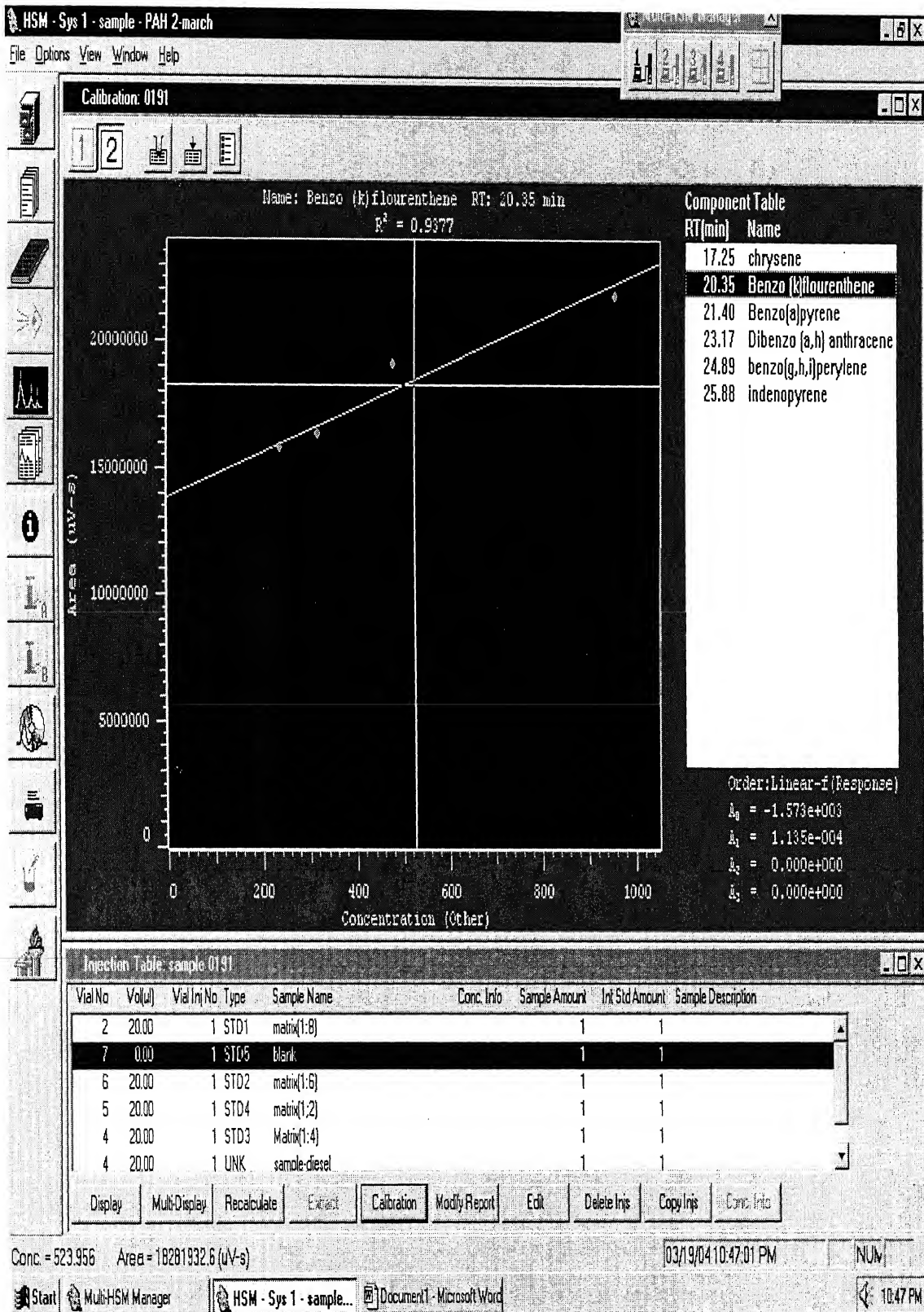


Fig C-2: Calibration Curve of Benzo(K) flouranthene

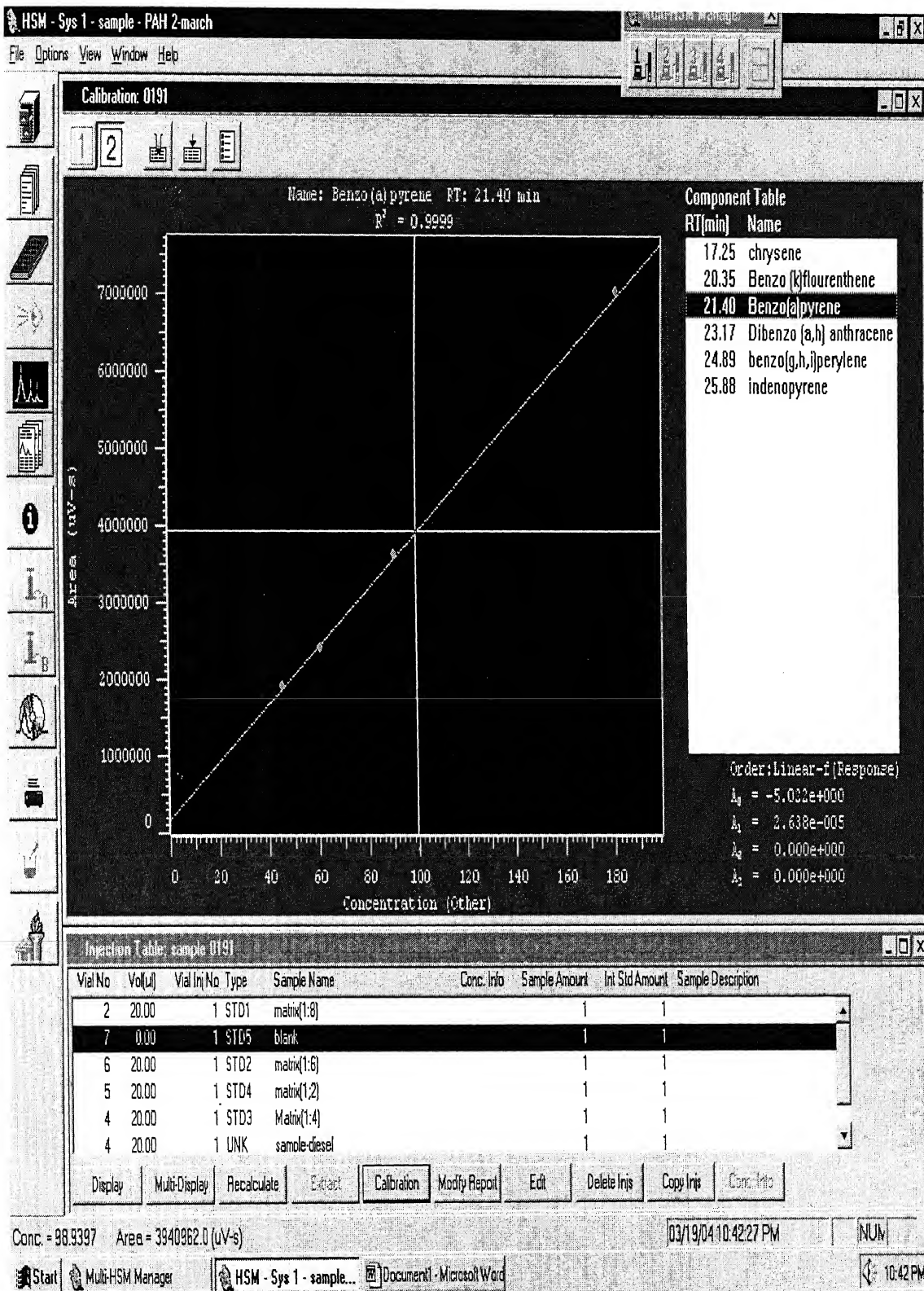


Fig C-3: Calibration Curve of Benzo(a) Pyrene

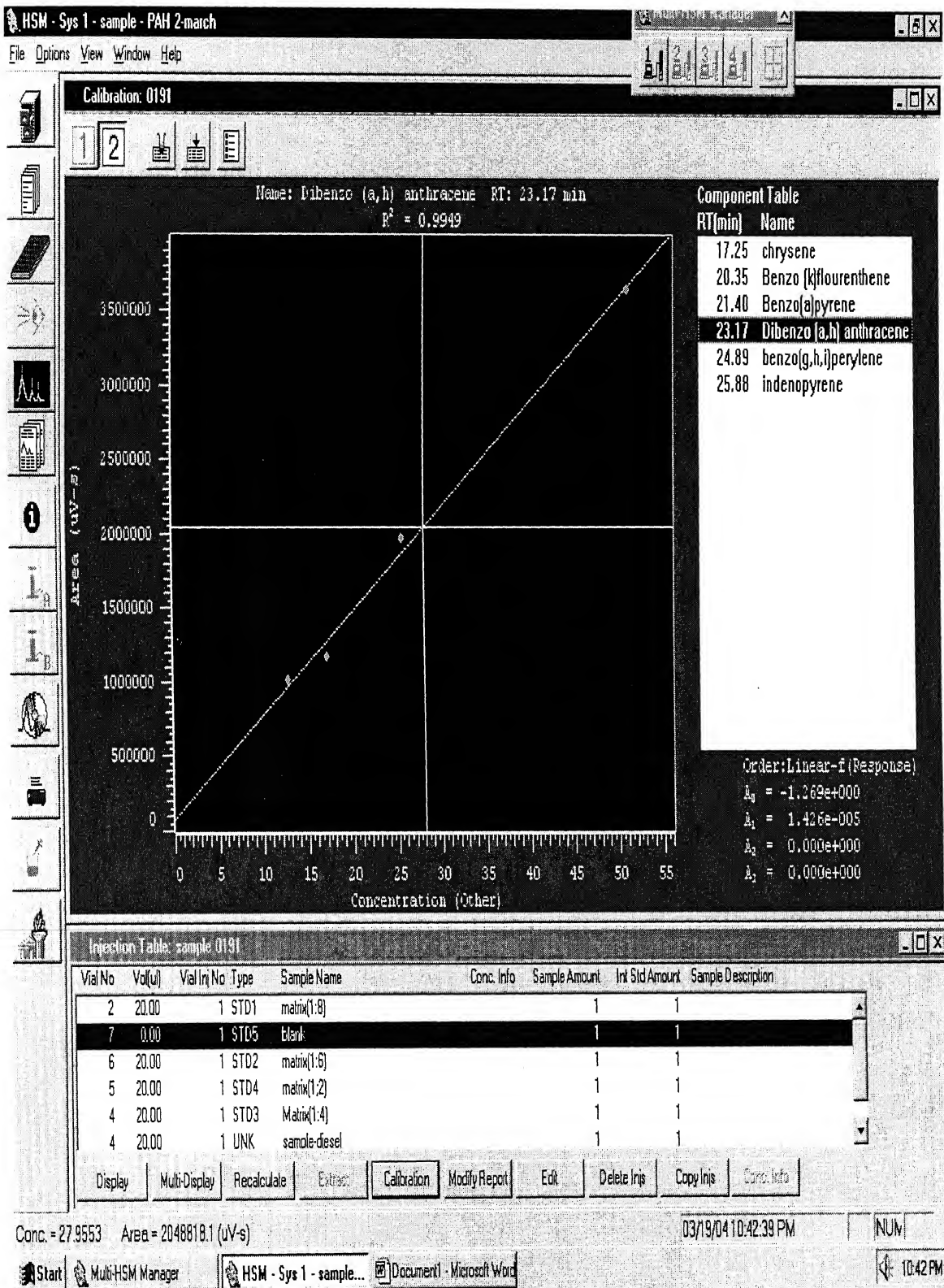


Fig C-4: Calibration Curve of Dibenzo (a,h) anthracene

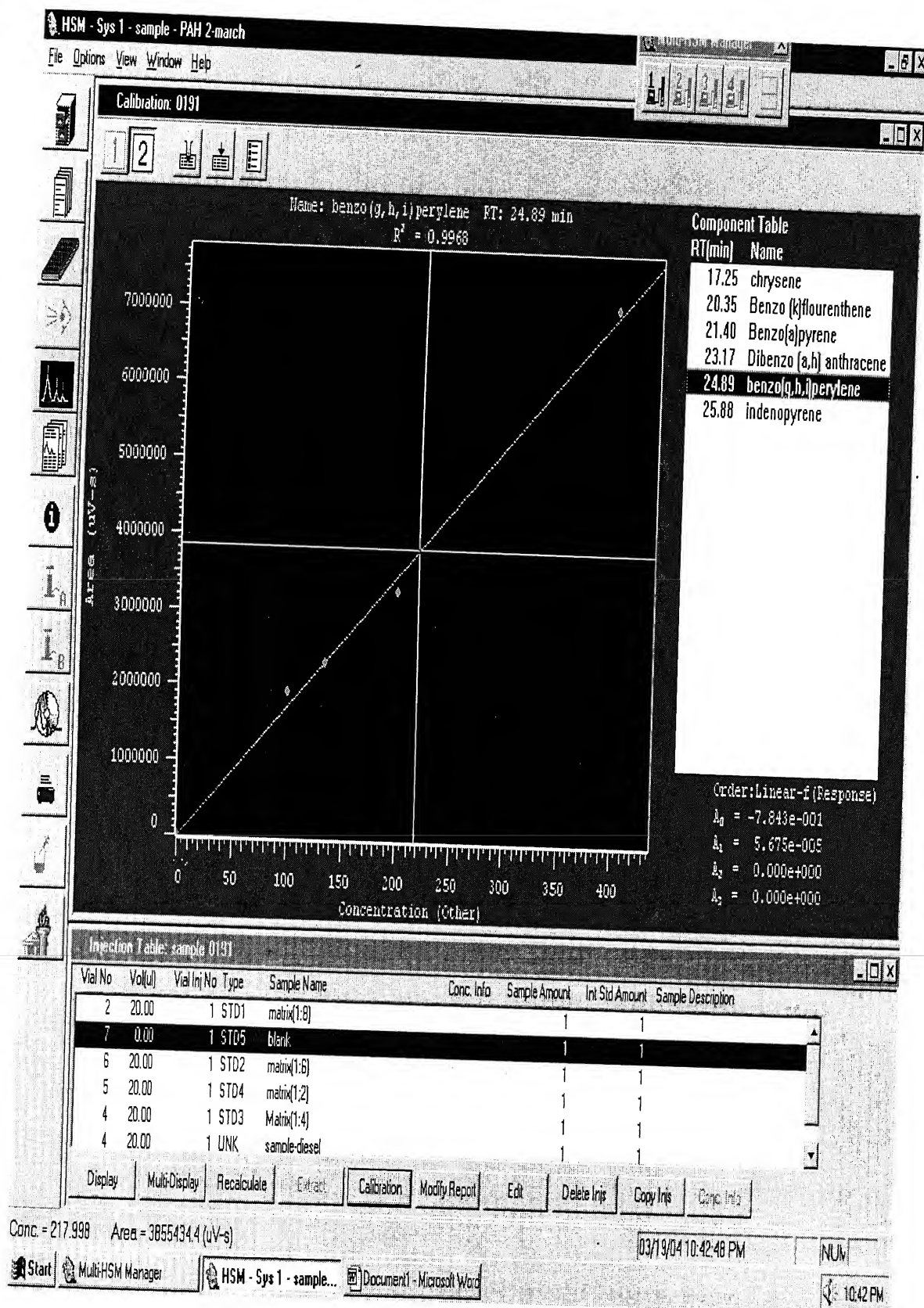


Fig C-5: Calibration Curve of Benzo (g,h,i) Perylene

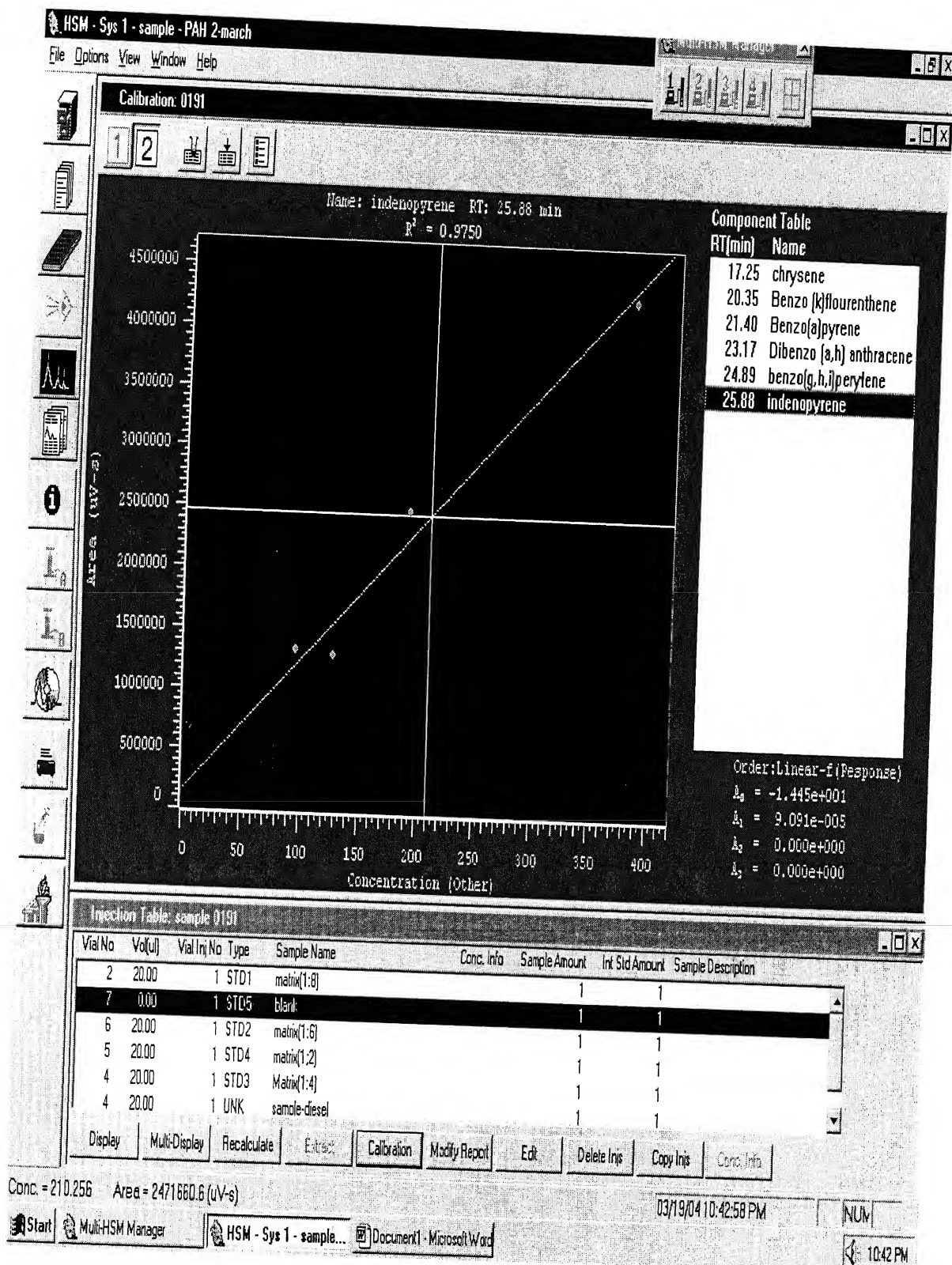


Fig C-6: Calibration Curve of Indenopyrene

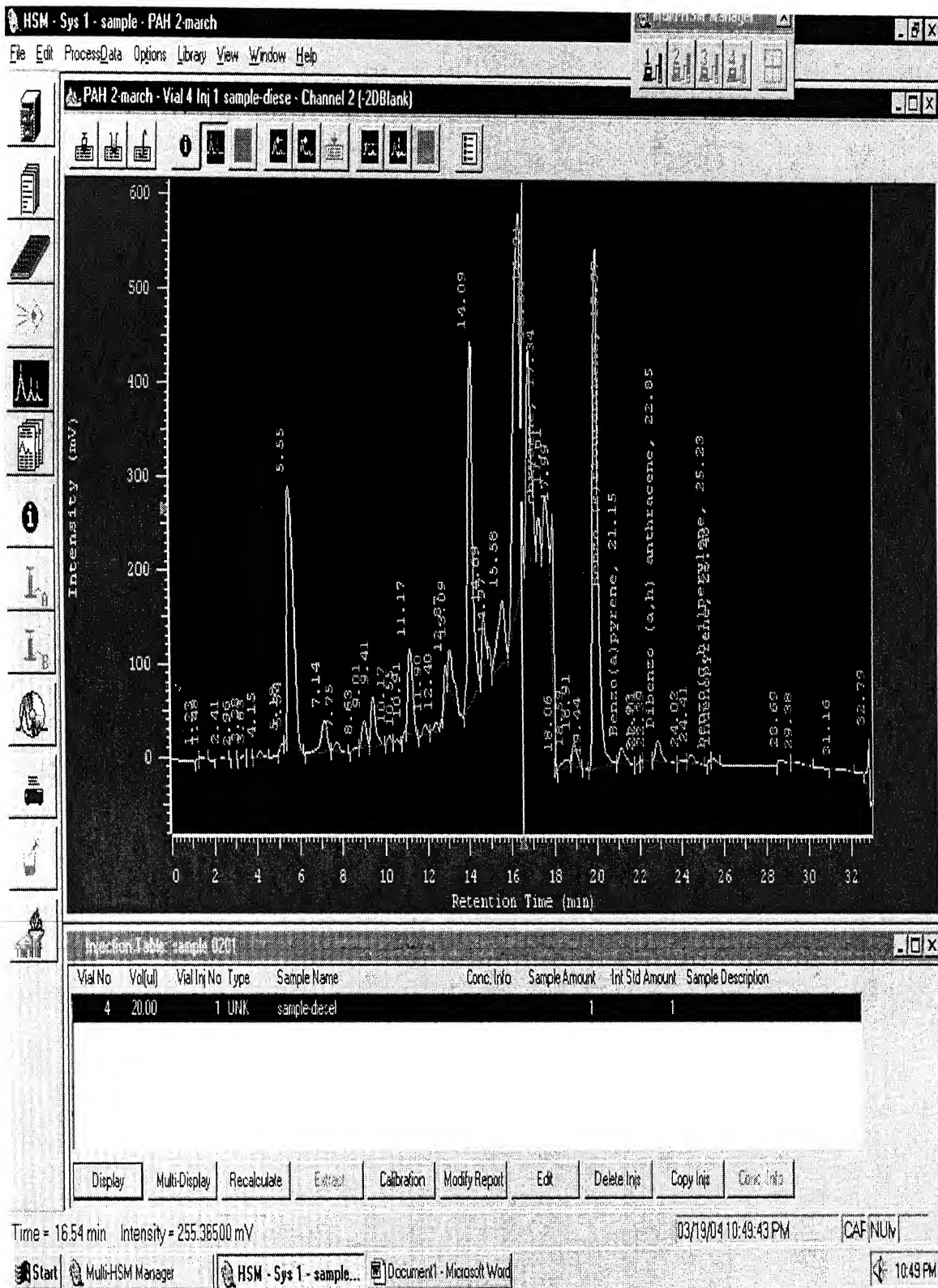
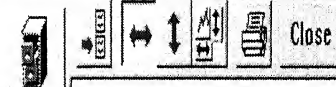


Fig C-7: PAHs in Particulates at Idle Load



D-7000 HSM: sample

Series: 0191

Report: modified

System: Sys 1

Vial Summary for Channel 2

Chrom Type: HPLC Channel : 2

Vial Number: 4

Name	Mean RT(min)	Conc 1 1	Mean CONC1
chrysene	16.84	181.484	181.484
Benzo (k)flourenthene	19.97	185.074	185.074
Benzo(a)pyrene	21.15	2.69133	2.69133
Dibenzo (a,h) anthracene	22.85	4.30805	4.30805
benzo(g,h,i)perylene	25.23	0.519452	0.519452
indenopyrene	25.48	-12.1356	-12.1356

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Column Oven: None

Pump A: L-7100

Number of Solvents pump A: 4

External Instrument Software: None

Autosampler: Manual

Pump B: None

Number of Solvents pump B: 1

Column Name: RP-18

Method Information:

Method Name: PAH 2-march

Description:

Developed by:

Pump Setup:

Main Pump (A) Pressure Limit: 0 to 412 bar

Pump A (L-7100):

Solvent A: acn

Solvent C: water

Solvent B: water

Solvent D: acn

Pump A (L-7100):

Pump Solvent and Event Table

Time (min)	%acn	%water	%water	%acn	Flow (ml/min)	Event 1	Event 2	Event 3	Event 4
0.0	60.0	40.0	0.0	0.0	1.000				
3.0	60.0	40.0	0.0	0.0					
15.0	100.0	0.0	0.0	0.0					
29.0	100.0	0.0	0.0	0.0					
29.1	60.0	40.0	0.0	0.0					
33.0	60.0	40.0	0.0	0.0					

Channel 2 Detector (L-7485):

Response Time: 2.0 s

PMT Voltage: Medium

Stop Time: 33.00 min

Initial Sampling Period: 200 ms

Offset: 0

Em Bandwidth: Standard

Auto Data Sampling Mode: YES

Doubling Time: 10.00 min

Detector Table

Time(min)	Ex. WL(nm)	Em. WL(nm)	Baseline
0.0	265	380	Auto Zero
18.0	265	380	Auto Zero
18.1	290	430	Auto Zero
22.0	290	430	Auto Zero
22.1	290	410	Auto Zero
25.2	290	410	Auto Zero
25.3	300	500	Auto Zero
28.5	300	500	Auto Zero

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CAF/NUV

Start

Multi-HSM Manager

HSM - Sys 1 - sample

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D-7000 HSM: sample

Series: 0201

Report: original

System: Sys 1

28.6	265	380	Auto Zero
33.0	265	380	Auto Zero

Sampling Period Table

Time(min)	Period(ms)
-----------	------------

0.00	200
10.00	400
30.00	800
70.00	1600
150.00	3200

Method DP for channel 2

Calculation Method:

Peak Quantitation: Area

Calculation Method: Ext Std

Concentration data from method.

Peak identification Window: % Time

STD peaks identification rule: Highest peak

UNK peaks identification rule: Closest peak

Calibration order of curve fit: Linear - f(Response)

Force through zero: NO

Minimum number of calibration levels required: 2

Concentration Weight: 1.0

Update RT in component Table: YES

Do blank subtraction: YES

Use blank from same series: NO

Blank Series name: 0185

Blank Sample name: Blank

Blank Sequence Number: 1

Blank Injection Number: 1

Do library search: NO

Component Table

RT (min)	Window (%)	Name	Func1	Func2	Func3
-------------	---------------	------	-------	-------	-------

17.25	10.00	chrysene			
20.35	5.00	Benzo (k)fluoreanthene			
21.40	10.00	Benzo(a)ovrene			
23.17	5.00	Dibenzo (a,h) anthracene			
24.89	10.00	benzo(a,h,i)perylene			
25.88	5.00	indenoovrene			

RT (min)	Mol. Weight	Multi- plier	E-Conc	Tolerance (%)
-------------	----------------	-----------------	--------	------------------

17.25	1.000	1.000		
20.35	1.000	1.000		
21.40	1.000	1.000		
23.17	1.000	1.000		
24.89	1.000	1.000		

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D-7000 HSM: sample

Series: 0201

Report: original

System: Sys 1

Concentration units: Other

Concentration Table:

Name	Std1	Std2	Std3	Std4	Std5
chrvsene	260.830	346.770	520.165	1040.33	0.000000
Benzo (k)flourenthene	238.850	318.470	477.705	955.410	0.000000
Benzo(a)bvrene	45.1100	60.1550	90.2300	180.465	0.000000
Dibenzo (a,h) anthracene	12.7380	16.9850	25.4775	50.9550	0.000000
benzo(a,h,i)perylene	99.2500	132.340	198.510	397.020	0.000000
indenopvrene	95.5400	127.380	191.080	382.165	0.000000

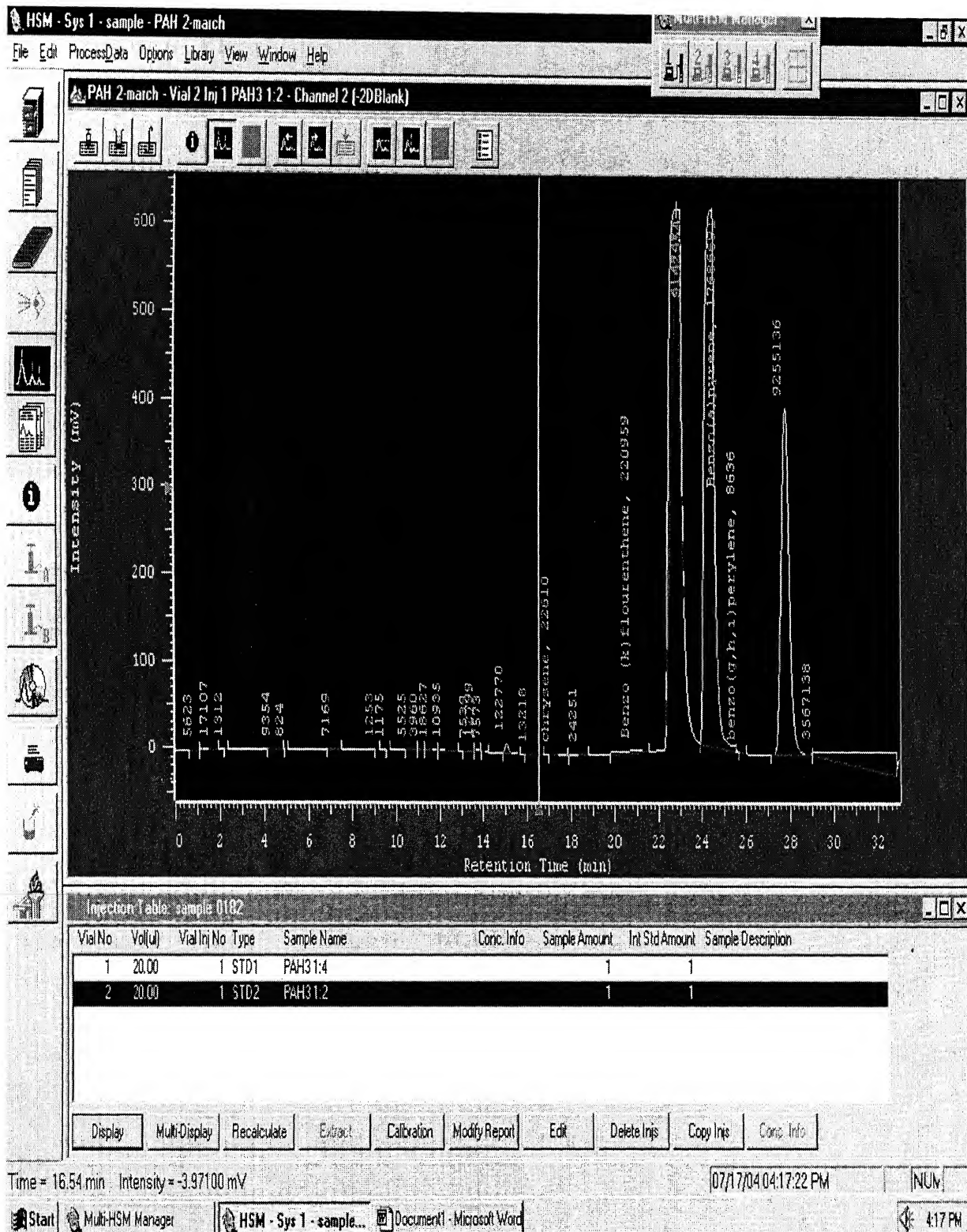
Coefficients table

Name	A0	A1	A2	A3
chrvsene	-3.534E+01	6.997E-05	0.000E+00	0.000E+00
Benzo (k)flourenthene	-1.266E+02	3.558E-05	0.000E+00	0.000E+00
Benzo(a)pyrene	-5.022E+00	2.638E-05	0.000E+00	0.000E+00
Dibenzo (a,h) anthracene	-1.269E+00	1.426E-05	0.000E+00	0.000E+00
benzo(a,h,i)perylene	-7.843E-01	5.675E-05	0.000E+00	0.000E+00
indenopvrene	-1.445E+01	9.091E-05	0.000E+00	0.000E+00

Name	Units	R-sqr
chrvsene	Other	0.9874
Benzo (k)flourenthene	Other	0.6680
Benzo(a)bvrene	Other	0.9999
Dibenzo (a,h) anthracene	Other	0.9949
benzo(a,h,i)perylene	Other	0.9968
indenopvrene	Other	0.9750

Integration Table

Time (min)	Function	Value/Status
0.00	NOISE	10
0.00	SMOOTHING	OFF
0.00	SENSITIVITY	20
0.00	N-METHOD	1



FigC-9: PAH in Particulates at 70% Load

Appendix D: Thimble Details

D.1: Details of Thimbles

Heavy Metal Sampling:

S.No	Load	Initial Wt. Of Thimble (g)	Final Wt. Of Thimble (g)	Wt. Of Particulates (g)
1	Idle	1.5124	1.5336	0.0212
		1.6231	1.6436	0.0205
2	40 %	1.7923	1.8275	0.0352
		1.6521	1.6916	0.0395
3	70%	1.5663	1.6065	0.0402
		1.6023	1.6461	0.0458
4	100%	1.6051	1.6532	0.0481
		1.7352	1.7854	0.0502

BSOF Sampling:

S.No	Load	Initial Wt. Of Thimble (g)	Final Wt. Of Thimble (g)	Wt. Of Particulates (g)	Wt.of beaker in (g)		Diff in (g)
					Initial Wt.	Final Wt.	
1	Idle	2.2965	2.5213	0.2248	29.2503	29.4008	0.1505
		2.6374	2.8479	0.2105	31.6850	31.8228	0.1378
2	40 %	2.1662	2.1685	0.0023	32.6763	32.6781	0.0018
		2.3561	2.3579	0.0018	31.2863	31.2878	0.0015
3	70%	2.8684	2.8749	0.0065	34.6359	34.6382	0.0023
		2.4672	2.4743	0.0071	33.8641	33.8668	0.0027
4	100%	2.2561	2.2633	0.0072	32.7352	32.7329	0.0024
		2.8325	2.8394	0.0069	33.6638	33.6606	0.0022

Elemental and Organic Carbon Sampling:

S.No	Load	Initial Wt. Of Thimble (g)	Final Wt. Of Thimble (g)	Wt. Of Particulates (g)
1	Idle	2.2552	2.6629	0.4077
2	40 %	1.9767	2.0092	0.0325
3	70%	2.1338	2.1804	0.0466

PAH Sampling:

Load	Initial wt. of thimble (g)	Final wt. of thimble (g)	diff (wt. of particulates) (g)
Idle	2.6872	2.9036	0.2164
40%	2.2439	2.2457	0.0018
70%	2.1885	2.1994	0.0059

D.2 : Blank Concentrations

S.No	Heavy Metal	Conc. in blank thimble, $\mu\text{g/g}$
1	Fe	43.11
2	Mg	25.83
3	Cr	ND
4	Ni	0.33
5	Pb	9.103
6	Zn	14.38
7	Ca	32.61
8	Ba	131.38

D.3 : Particulate Concentrations

Engine Load	Particulate Concentration, $\mu\text{g/m}^3$
Idle	50000
40%	90000
70%	102380.95
100%	136190.47